Inorg. Chem. **2008**, *47*, 10662−10673

Inorganic Chemistry

Article

Dinuclear Copper(I) and Copper(I)/Silver(I) Complexes with Condensed Dithiolato Ligands[1]

José Vicente,[†] Pablo González-Herrero,*,[†] Yolanda García-Sánchez,[†] and Delia Bautista[‡]

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain, and SAI, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain

Received July 28, 2008

The Cu(III) complex $Pr_4N[Cu\{S_2C{=}(t\text{-Bu-fy})\}_2]$ (**1**) (*t*-Bu-fy = 2,7-di-*tert*-butylfluoren-9-ylidene) reacts with $[Cu(PR_3)_4]ClO_4$ in 1:1 molar ratio in MeCN to give the dinuclear complexes $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_n]$ [n = 2, R = Ph (**2a**); n = 3, R = To (**3b**); To = *p*-tolyl]. The analogue of **2a** with R = To (**2b**) can be obtained from the reaction of **3b** with 1/8 equiv of S_8. Compound **2b** establishes a thioketene-exchange equilibrium in solution leading to the formation of $[Cu_4\{S_2C{=}(t\text{-Bu-fy})\}_2(PTo_3)_4]$ (**4b**) and $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_3S\}(PTo_3)_2]$ (**5b**). Solid mixtures of **4b** and **5b** in varying proportions can be obtained when the precipitation of **2b** is attempted using MeCN. The reactions of **1** with $AgClO_4$ and PPh_3, PTo_3 or PCy_3 in 1:1:4 molar ratio in MeCN afford the heterodinuclear complexes $[AgCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_3]$ [R = Ph (**6a**), To (**6b**), Cy (**6c**)]. Complex **6c** dissociates PCy_3 in solution to give the bis(phosphine) derivative $[AgCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**7c**), which undergoes the exchange of $[M(PCy_3)]^+$ units in CD_2Cl_2 solution to give small amounts of $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**2c**) and $[Ag_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**8c**). Complexes **6a** and **b** participate in a series of successive equilibria in solution, involving the dissociation of phosphine ligands and the exchange of $[M(PCy_3)]^+$ units to give **2a** or **3b** and the corresponding disilver derivatives $[Ag_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_2]$ [R = Ph (**8a**), To (**8b**)], followed by thioketene-exchange reactions to give $[AgCu\{[SC{=}(t\text{-Bu-fy})]_3S\}(PR_3)_2]$ [R = Ph (**9a**), To (**9b**)]. Complexes **9a** and **b** can be directly prepared from the reactions of **1** with $AgClO_4$ and PPh_3 or PTo_3 in 1:1:3 molar ratio in THF. The crystal structures of **3b**, **6b**, **6c**, **7c**, and **9a** have been solved by single-crystal X-ray diffraction studies and, in the cases of **7c** and **9a**, reveal the formation of short Ag···Cu metallophilic contacts of 2.8157(4) and 2.9606(6) Å, respectively.

Introduction

One of our research interests concerns the synthesis of metal complexes with 1,1-ethylenedithiolato ligands and the study of their structures and chemical and photophysical properties. We have reported the synthesis of mononuclear Au,[2−4] Tl,[3] Pd,[5,6] Pt,[6−8] and Cu[9] and homo- and heteropolynuclear M/M′ (M = Pd, Pt, M′ = Au, Ag;[7,10] M = Pd, Pt, M′ = Ni, Cd, Hg;[10] M = Pd, Pt, M′ = Au[6]) derivatives.

Polynuclear copper complexes with thiolato ligands are of interest as models for the understanding of the structure, bonding, and function of the active sites of copper−sulfur enzymes and proteins.[11] Silver thiolato complexes often exhibit similar coordination environments to those of their copper analogues, and the study of their structures and spectroscopic features is relevant to the research concerning the metal-binding sites of copper metallothioneins and the toxicology of silver and silver-based therapeutic agents.[12]

---

* To whom correspondence should be addressed. E-mail: pgh@um.es.
[†] Facultad de Química, Universidad de Murcia.
[‡] SAI, Universidad de Murcia.

(1) (Fluoren-9-ylidene)methanedithiolato complexes. Part 5. For previous parts, see refs, 4, 6, 8 and 9.

(2) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Jones, P. G. *Chem. Commun.* **1997**, 2047–2048.

(3) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Inorg. Chem.* **1999**, *38*, 5018–5026.

(4) Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bardají, M. *Inorg. Chem.* **2004**, *43*, 7516–7531.

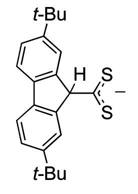
(5) Vicente, J.; Chicote, M. T.; Martínez-Viviente, E.; Martínez-Martínez, A. J.; Jones, P. G. *Inorg. Chem.* **2006**, *45*, 10434–10436.

(6) Vicente, J.; González-Herrero, P.; Pérez-Cadenas, M.; Jones, P. G.; Bautista, D. *Inorg. Chem.* **2007**, *46*, 4718–4732.

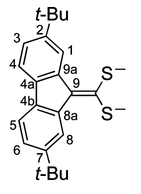
(7) (a) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K *Inorg. Chem.* **2001**, *40*, 2051–2057. (b) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G. *Inorg. Chem.* **2003**, *42*, 4268–4274.

10.1021/ic8014139 CCC: $40.75

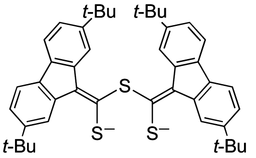
Chart 1



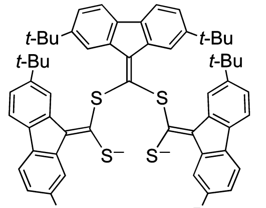
I
$(t\text{-Bu-Hfy})CS_2^-$



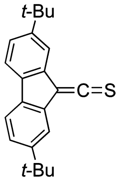
II
$(t\text{-Bu-fy})=CS_2^{2-}$



III
$\{S[(t\text{-Bu-fy})=CS]_2\}^{2-}$

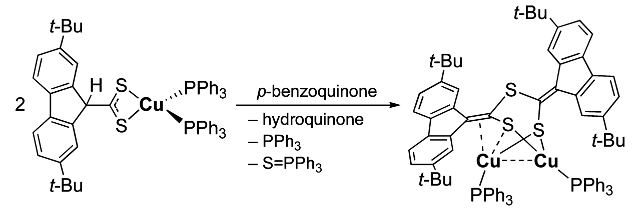


IV
$\{S[(t\text{-Bu-fy})=CS]_3\}^{2-}$



V
$(t\text{-Bu-fy})=CS$

Scheme 1



We have recently described the synthesis of a series of copper complexes with 2,7-di-*tert*-butyl-9*H*-fluorene-9-carbodithioate [$(t\text{-Bu-Hfy})CS_2^-$, **I**, Chart 1] and (2,7-di-*tert*-butylfluoren-9-ylidene)methanedithiolate [$(t\text{-Bu-fy})=CS_2^{2-}$, **II**].[9] (Fluoren-9-ylidene)methanedithiolate ligands like **II** show remarkable differences with respect to those most frequently used 1,1-ethylenedithiolato ligands containing strong electron-withdrawing substituents that affect the redox and photophysical properties of their metal complexes.[4,8] Thus, we have reported that the aerial oxidation of Cu(I) and Cu(II) complexes containing ligand **II** afford the copper(III) complex $[Cu\{S_2C=(t\text{-Bu-fy})\}_2]^-$ (**1**),[9] while the only previously reported 1,1-ethylenedithiolato Cu(III) complex $[Cu(ded)_2]^-$ [ded = $(EtO_2C)_2C=CS_2^{2-}$] was prepared by oxidation of a Cu(II) precursor with H_2O_2, I_2, or Cu^{2+} ions.[13] The relatively milder conditions required for the preparation of **1** can be connected to the stronger electron-donating character of ligand **II** as compared to ded. In addition, we have shown that upon deprotonation of Cu(I) dithioato complexes of the type $[Cu\{S_2C(t\text{-Bu-Hfy})\}(PR_3)_2]$ in the presence of a base, or through their reaction with *p*-benzoquinone, dinuclear complexes containing the condensed dithiolato ligand $\{S[(t\text{-Bu-fy})=CS]_2\}^{2-}$ (**III**) are obtained (Chart 1, Scheme 1). This type of reaction had not been observed for other dithioato complexes of the type $[Cu(S_2CR)(PR'_3)_2]$. We concluded that both the presence of the relatively acidic H9 hydrogen atom in ligand **I** and the electron-donating ability of ligand **II** are crucial for the initial deprotonation/oxidation steps leading to the formation of the condensed ligand **III**.

As part of our research in the field of heteropolynuclear complexes with 1,1-ethylenedithiolato ligands, we report here the reactions of the Cu(III) complex **1** with Cu(I) or Ag(I) phosphino complexes and show that the coordination of **1** to Cu(I) or Ag(I) ions triggers the reduction of the Cu(III) center leading to dinuclear Cu(I) or Cu(I)/Ag(I) complexes containing the condensed ligand **III**, with concomitant formation of phosphine sulfide. In certain cases, subsequent processes lead to the formation of dinuclear complexes with the ligand $\{S[(t\text{-Bu-fy})=CS]_3\}^{2-}$ (**IV**), resulting from the exchange of units of the thioketene compound $(t\text{-Bu-fy})=CS$ (**V**, Chart 1).

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. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $Pr_4N[Cu\{S_2C=(t\text{-Bu-fy})\}_2]$[9] (**1**), $[Cu(PR_3)_4]ClO_4$ (R = Ph, To), and $[Ag(PPh_3)_4]ClO_4$[14] were prepared following published procedures. All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers usually at 298 K, unless otherwise indicated. Chemical shifts are referred to internal TMS (^1H and $^{13}C\{H\}$) or external 85 % H_3PO_4 ($^{31}P\{H\}$). $^{13}C\{H\}$ NMR spectra were recorded only for those compounds which do not undergo rapid exchange processes at room temperature. The assignments of the ^1H and $^{13}C\{H\}$ NMR spectra were made with the help of HMBC and HSQC experiments. Chart 1 shows the atom numbering of the

---

(8) Vicente, J.; González-Herrero, P.; Pérez-Cadenas, M.; Jones, P. G.; Bautista, D. *Inorg. Chem.* **2005**, *44*, 7200–7213.

(9) Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bautista, D. *Eur. J. Inorg. Chem.* **2006**, 115–126.

(10) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 6193–6200.

(11) (a) Tolman, W. B. *J. Biol. Inorg. Chem.* **2006**, *11*, 261–271. (b) Henkel, G.; Krebs, B. *Chem. Rev.* **2004**, *104*, 801–824. (c) Fujisawa, K.; Imai, S.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 168–169. (d) Hanss, J.; Kruger, H. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 2827–2830.

(12) (a) Salgado, M. T.; Bacher, K. L.; Stillman, M. J. *J. Biol. Inorg. Chem.* **2007**, *12*, 294–312. (b) Palacios, O.; Polec-Pawlak, K.; Lobinski, R.; Capdevila, M.; Gonzalez-Duarte, P. *J. Biol. Inorg. Chem.* **2003**, *8*, 831–842. (c) Fujisawa, K.; Imai, S.; Suzuki, S.; Moro-oka, Y.; Miyashita, Y.; Yamada, Y.; Okamoto, K.-i. *J. Inorg. Biochem.* **2000**, *82*, 229–238. (d) Stillman, M. J. *Metal Based Drugs* **1999**, *6*, 277–290. (e) Zelazowski, A. J.; Gasyna, Z.; Stillman, M. J. *J. Biol. Chem.* **1989**, *264*, 17091–17099. (f) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed.* **1991**, *30*, 769–788.

(13) (a) Hollander, F. J.; Caffery, M. L.; Coucouvanis, D. *J. Am. Chem. Soc.* **1974**, *96*, 4682–4684. (b) Coucouvanis, D.; Hollander, F. J.; Caffery, M. L. *Inorg. Chem.* **1976**, *15*, 1853–1860.

(14) (a) Cotton, F. A.; Goodgame, D. M. L. *J. Chem. Soc.* **1960**, 5267–5269. (b) Cingolani, A.; Effendy; Marchetti, F.; Pettinari, C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4047–4055.

Table 1. Crystallographic Data for **3b**, **6b**, **6c**·2CH$_2$Cl$_2$, **7c**·0.82MeCN·0.18CH$_2$Cl$_2$ and **9a**·CHCl$_3$

	3b	**6b**	**6c**·2CH$_2$Cl$_2$	**7c**·0.82MeCN·0.18CH$_2$Cl$_2$	**9a**·CHCl$_3$
formula	$C_{107}H_{111}Cu_2P_3S_3$	$C_{107}H_{111}AgCuP_3S_3$	$C_{100}H_{151}AgCl_4CuP_3S_3$	$C_{81.82}H_{116.82}AgCl_{0.36}$ $CuN_{0.82}P_2S_3$	$C_{103}H_{113}AgCl_3CuP_2S_4$
fw	1713.13	1757.42	1855.51	1454.29	1808.79
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	14.0816(4)	14.2036(8)	15.1117(9)	14.0694(11)	13.0519(5)
b (Å)	19.5672(5)	19.6400(12)	25.9909(16)	16.7786(12)	14.8549(5)
c (Å)	32.9459(9)	32.886(2)	25.8898(16)	18.5545(13)	23.7462(9)
α (deg)	90	90	90	66.222(2)	88.700(2)
β (deg)	95.330(2)	95.224(2)	106.858(2)	77.685(2)	84.589(2)
γ (deg)	90	90	90	70.460(2)	77.899(2)
V (Å^3)	9038.6(4)	9135.8(10)	9731.7(10)	3761.8(5)	4481.6(3)
Z	4	4	4	2	2
ρ_{calcd} (Mg m^{-3})	1.259	1.278	1.266	1.284	1.340
μ (mm^{-1})	0.641	0.616	0.687	0.724	0.722
R1^a	0.0864	0.0569	0.0443	0.0453	0.0718
wR2^b	0.1865	0.1218	0.1042	0.1147	0.1409

[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.

fluoren-9-ylidene group. 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 FT-IR spectrophotometer using Nujol mulls between polyethylene sheets or KBr pellets.[15]

X-ray Structure Determinations. Crystals of **3b**, **6b**, **6c**·2CH$_2$Cl$_2$, **7c**·0.2CH$_2$Cl$_2$·0.8MeCN, and **9a**·CHCl$_3$ suitable for X-ray diffraction studies were obtained from CH$_2$Cl$_2$/MeOH (**3b**), CH$_2$Cl$_2$/MeCN (**6b**, **6c**, **7c**), or CHCl$_3$/pentane (**9a**). Numerical details are presented in Table 1. The data were collected on a Bruker Smart APEX diffractometer using monochromated Mo-Kα radiation in ω-scan mode. The structures were solved by direct methods, except for **9a**, which was solved by the Patterson method. All of them were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Restraints to local aromatic ring symmetry or light-atom displacement factor components were applied in some cases. The hydrogen atoms were refined using rigid methyl groups or a riding model. *Special features of refinement:* For compounds **3b**, **6c** and **9a**, the Me groups of one, two, or three of the *t*-Bu groups, respectively, are disordered over two positions. The solvent in the crystals of **6c** was so badly resolved that no sensible refinement model could be developed. For this reason the program SQUEEZE (Prof. 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 two CH$_2$Cl$_2$ molecules was assumed. For compound **7c**, an ill-defined region of residual electron density was interpreted as the superposition of CH$_2$Cl$_2$ and MeCN (~18:82), and their hydrogen atoms were not included in the refinement.

[Cu$_2${[SC=(*t*-Bu-fy)]$_2$S}(PPh$_3$)$_2$] (2a). A solid mixture of Pr$_4$N[Cu{S$_2$C=(*t*-Bu-fy)}$_2$] (**1**) (131 mg, 0.14 mmol) and [Cu(PPh$_3$)$_4$]ClO$_4$ (167 mg, 0.14 mmol) was suspended in MeCN and stirred for 22 h. The color of the suspension gradually changed from green to yellow. The yellow precipitate was filtered off, washed with MeCN (2 × 5 mL), and vacuum-dried to give **2** as an orange solid. Yield: 163 mg, 89%. The spectroscopic and analytical data for this complex have been previously reported.[9]

[Cu$_2${[SC=(*t*-Bu-fy)]$_2$S}(PTo$_3$)$_2$] (2b). A solution of **3b** (103 mg, 0.06 mmol) and S$_8$ (2 mg, 0.01 mmol) in CH$_2$Cl$_2$ (8 mL) was stirred for 16 h and filtered through Celite. Partial evaporation of the filtrate (1 mL) and addition of MeOH (20 mL) led to the precipitation of a red solid, which was filtered off, recrystallized from CH$_2$Cl$_2$/MeOH, and vacuum-dried to give **2b**. Yield: 60 mg, 71%. Anal. Calcd for C$_{85}$H$_{90}$Cu$_2$P$_2$S$_3$: C, 73.32; H, 6.44; S, 6.83. Found: C, 73.26; H, 6.51; S, 6.39. Mp: 150 °C (dec). IR (KBr, cm^{-1}): ν(C=CS$_2$), 1498, 1484, 1456. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 9.58, 8.61 (both d, $^4J_{HH}$ = 1.6 Hz, 1 H each, H1/H8), 7.47, 7.43 (both d, $^3J_{HH}$ = 8.0 Hz, 2 H each, H4, H5), 7.22, 7.19 (both dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H each, H3, H6), 6.95 (m, 12 H, To), 6.72 (d, $^3J_{HH}$ = 7.2 Hz, 12 H, To), 2.22 (s, 18 H, Me, To), 1.23, 1.15 (both s, 18 H each, *t*-Bu). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 148.9, 148.7 (C2, C7), 140.3 (C8a, C9a), 139.6 (*p*-C, To), 139.2 (C8a, C9a), 136.5, 136.2 (C4a, C4b), 133.5 (d, $^2J_{CP}$ = 15 Hz, *o*-C, To), 131.8 (C9), 129.2 (d, $^3J_{CP}$ = 10 Hz, *m*-C, To), 128.1 (d, $^1J_{CP}$ = 41 Hz, *i*-C, To), 123.8, 123.7, 123.0, 122.9 (C1, C3, C6, C8), 117.9, 117.7 (C4, C5), 34.9, 34.8 (*C*Me$_3$), 31.6, 31.4 (C*Me*$_3$), 21.3 (Me, To); *C*S$_2$ not observed. ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$): δ 5.1 (br).

[Cu$_2${[SC=(*t*-Bu-fy)]$_2$S}(PTo$_3$)$_3$] (3b). A solid mixture of **1** (193 mg, 0.20 mmol) and [Cu(PTo$_3$)$_4$]ClO$_4$ (278 mg, 0.20 mmol) was suspended in MeCN (20 mL) and stirred for 8.5 h. An orange precipitate gradually formed, which was filtered off, recrystallized from CH$_2$Cl$_2$ (5 mL)/MeCN (70 mL) and vacuum-dried to give **3b**. Yield: 274 mg, 79 %. Anal. Calcd for C$_{107}$H$_{111}$Cu$_2$P$_3$S$_3$: C, 75.01; H, 6.53; S, 5.61. Found: C, 74.51; H, 6.74; S, 5.44. Mp: 196 °C (dec). IR (KBr, cm^{-1}): ν(C=CS$_2$), 1497, 1483, 1454. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 9.58 (s, 2 H, H1/H8), 8.58 (d, $^4J_{HH}$ = 1.5 Hz, 2 H, H1/H8), 7.48, 7.44 (both d, $^3J_{HH}$ = 8.0 Hz, 2 H each, H4, H5), 7.21, 7.18 (both dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H each, H3, H6), 7.04 (br m, 18 H, To), 6.82 (br, 18 H, To), 2.23 (s, 27 H, Me, To), 1.18, 1.17 (both s, 18 H each, *t*-Bu). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$, 298 K): δ 4.8 (br). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$, 213 K): δ −0.33 (s), −0.46, −6.62 (AB system, $^2J_{AB}$ = 117.8 Hz).

Reaction of 1 with [Cu(NCMe)$_4$]PF$_6$ and PTo$_3$. Procedure A. To a solid mixture of **1** (165 mg, 0.17 mmol), [Cu(NCMe)$_4$]PF$_6$ (64 mg, 0.17 mmol), and PTo$_3$ (179 mg, 0.59 mmol) was added tetrahydrofuran (THF, 15 mL), and the resulting solution was stirred for 20 h. The color of the solution gradually changed from dark brown to red. The solvent was evaporated to dryness and the residue was dissolved in CH$_2$Cl$_2$ (15 mL). The turbid red solution was filtered through Celite to remove insoluble impurities and concen-

---

[15] For several of the Ag/Cu compounds, the pellets were extracted with CDCl$_3$ and the ^{1}H NMR spectra showed no decomposition.

trated (8 mL). The addition of MeOH (40 mL) led to the precipitation of the dithiolato complex $[Cu_4\{S_2C{=}(t\text{-Bu-fy})\}_2(PTo_3)_4]\cdot 0.5CH_2Cl_2$ (**4b**) as a yellow solid, which was filtered off, washed with MeOH (2 mL), and vacuum-dried. Partial evaporation of the red filtrate (20 mL) led to the precipitation of **2b** as a red solid, which was filtered off, washed with MeOH (2 × 2 mL), and vacuum-dried. Yield: 30 mg of **4b**, 16 %; 128 mg of **2b**, 54%, based on Cu.

Procedure B. A solid mixture of **1** (203 mg, 0.21 mmol), $[Cu(NCMe)_4]PF_6$ (80 mg, 0.21 mmol), and PTo_3 (201 mg, 0.66 mmol) was suspended in MeCN (20 mL) and stirred for 23 h. The solvent was evaporated under reduced pressure, and the dark red residue was treated with CH_2Cl_2 (20 mL). The resuting turbid red solution was filtered through Celite to remove insoluble impurities and concentrated (8 mL). The addition of MeCN (60 mL) led to the slow precipitation of a dark green solid, which was filtered off, washed with MeCN (2 × 2 mL), and vacuum-dried. According to its IR and NMR data, this solid is a mixture of **4b** and $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_3S\}(PTo_3)_2]$ (**5b**). Yield: 99 mg. Variable proportions of the two components were obtained in different preparations (molar ratio **4b**:**5b** from 1:1 to 1:3.6); the IR and NMR data for **5b** were obtained using one of the mixtures with higher content of this complex.

Data for 4b. Anal. Calcd for $C_{128.5}H_{133}ClCu_4P_4S_4$: C, 69.55; H, 6.04; S, 5.78. Found: C, 69.28; H, 6.24; S, 5.49. Mp: 167 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1488, 1456. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.41 (d, $^4J_{HH} = 1.6$ Hz, 2 H, H1, H8), 7.65 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H4, H5), 7.19 (dd, $^4J_{HH} = 1.6$ Hz, $^3J_{HH} = 8.0$ Hz, 2 H, H3, H6), 7.08 (m, 12 H, To), 6.50 (d, $^3J_{HH} = 7.2$ Hz, 12 H, To), 2.00 (s, 18 H, Me, To), 0.96 (s, 18 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 147.7 (C2, C7), 141.2 (C8a, C9a), 138.8 (*p*-C, To), 135.4 (C4a, C4b), 133.8 (d, $^2J_{CP} = 15$ Hz, *o*-C, To), 132.8 (C9), 129.9 (d, $^1J_{CP} = 32$ Hz, *i*-C, To), 129.0 (d, $^3J_{CP} = 10$ Hz, *m*-C, To), 125.1 (C1, C8), 120.9 (C3, C6), 116.9 (C4, C5), 34.6 (CMe_3), 31.6 (CMe_3), 21.2 (Me, To); CS_2 not observed. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ −6.1 (s).

Data for 5b. IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1499, 1474. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.28, 8.58, 8.34 (all d, $^4J_{HH} = 1.5$ Hz, 2 H each, H1, H8), 7.61, 7.58 (both d, $^3J_{HH} = 8.0$ Hz, 2 H each, H4, H5), 7.25, 7.21, 7.08 (all dd, $^4J_{HH} = 1.6$ Hz, $^3J_{HH} = 8.0$ Hz, 2 H each, H3, H6), 7.03 (m, 6 H, To), 7.01 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H4, H5), 6.90 (m, 6 H, To), 6.73, 6.42 (both br d, $^3J_{HH} = 6.8$ Hz, 6 H each, To), 2.23, 2.02 (both s, 9 H each, Me, To), 1.33, 1.16, 0.83 (all s, 18 H each, *t*-Bu). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 0.2, −3.0 (both br).

[AgCu{[SC=(*t*-Bu-fy)]$_2$S}(PPh$_3$)$_3$] (6a). A solid mixture of **1** (354 mg, 0.37 mmol), $AgClO_4$ (77 mg, 0.37 mmol), and PPh_3 (394 mg, 1.50 mmol) was supended in MeCN (20 mL) and stirred for 3 days. A yellow precipitate gradually formed, which was filtered off, washed with MeCN (2 × 3 mL) and vacuum-dried to give **6a**. Yield: 595 mg, 98%. Anal. Calcd for $C_{98}H_{93}AgCuP_3S_3$: C, 72.15; H, 5.75; S, 5.90. Found: C, 72.20; H, 5.85; S, 5.56. Mp: 127 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1517, 1488, 1458. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.81, 9.43, 8.54, 8.47 (all br, 1 H each, H1, H8), 7.65 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H4, H5), 7.43 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.8$ Hz, 2 H, H3, H6), 7.30−6.94 (br m, 34 H, H4, H5, H3, H6 + Ph), 1.23, 1.19, 1.14, 0.98 (all s, 9 H each, *t*-Bu). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 4.5 (br).

[AgCu{[SC=(*t*-Bu-fy)]$_2$S}(PTo$_3$)$_3$] (6b). A solid mixture of **1** (145 mg, 0.15 mmol), $AgClO_4$ (33 mg, 0.16 mmol), and PTo_3 (190 mg, 0.62 mmol) was suspended in MeCN (15 mL) and stirred for 23 h. An orange precipitate gradually formed, which was separated by filtration and dissolved in CH_2Cl_2 (10 mL). The turbid red solution was filtered through Celite to remove insoluble impurities and concentrated (5 mL). The addition of MeCN (40 mL) led to the precipitation of an orange solid, which was filtered off, washed with MeCN (2 × 3 mL), and vacuum-dried to give **6b**. Yield: 190 mg, 71%. Anal. Calcd for $C_{107}H_{11}AgCuP_3S_3$: C, 73.12; H, 6.37; S, 5.47. Found: C, 73.00; H, 6.51; S, 5.43. Mp: 196 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1497, 1482, 1453. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.79, 9.38, 8.47, 8.45 (all br, 1 H each, H1, H8), 7.64 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H4, H5), 7.42, 7.41 (both d, $^3J_{HH} = 8.0$ Hz, 1 H each, H4, H5), 7.27−7.12 (m, 4 H, H3, H6), 7.08 (br m, 24 H, To), 6.85 (br m, 24 H, To), 2.23 (s, 27 H, Me, To), 1.25, 1.20, 1.16, 0.93 (all s, 9 H each, *t*-Bu). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 3.1 (br).

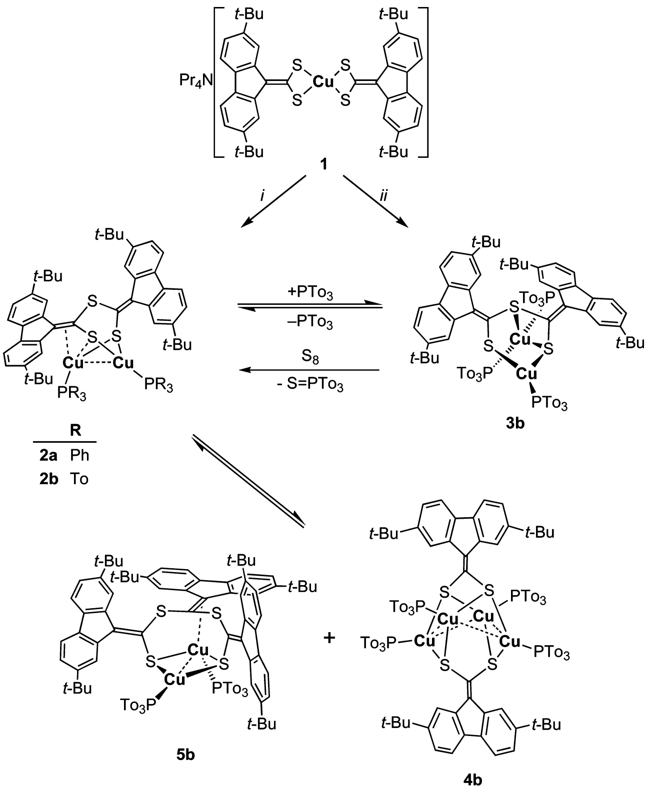
[AgCu{[SC=(*t*-Bu-fy)]$_2$S}(PCy$_3$)$_3$] (6c). The compound **6c**$\cdot$1.5CH_2Cl_2 was obtained as an orange solid following the procedure described for **6b**, starting from **1** (282 mg, 0.30 mmol), $AgClO_4$ (63 mg, 0.30 mmol), and PCy_3 (378 mg, 1.35 mmol). Yield: 450 mg, 84%. Anal. Calcd for $C_{99.5}H_{150}AgCl_3CuP_3S_3$: C, 65.91; H, 8.34; S, 5.31. Found: C, 66.12; H, 8.59; S, 5.15. Mp: 111 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1502, 1484, 1447. ^1H NMR (400.9 MHz, CD_2Cl_2, 213 K): δ 9.90, 9.72, 8.57, 8.16 (all s, 1 H each, H1/H8), 7.67, 7.64, 7.52, 7.42 (all d, $^3J_{HH} = 8.0$ Hz, 1 H each, H4/H5), 7.26, 7.21, 7.10, 7.00 (all d, $^3J_{HH} = 8.0$ Hz, 1 H each, H3/H6), 1.85−1.40 (br m, 63 H, Cy), 1.33, 1.31, 1.21 (all s, 9 H each, *t*-Bu), 1.20−0.8 (br m, 36 H, Cy), 0.62 (s, 9 H, *t*-Bu). $^{31}P\{^1H\}$ NMR (162.3 MHz, CD_2Cl_2, 213 K): δ 25.0 (A parts of 2 ABX systems, $^2J_{A\text{-}B} = 117$ Hz, $^1J_{P\text{-}^{107}Ag} = 418$ Hz, $^1J_{P\text{-}^{109}Ag} = 484$ Hz), 19.2 (s), 16.6 (B parts of 2 ABX systems, $^1J_{P\text{-}^{107}Ag} = 340$ Hz, $^1J_{P\text{-}^{109}Ag} = 392$ Hz).

[AgCu{[SC=(*t*-Bu-fy)]$_2$S}(PCy$_3$)$_2$] (7c). To a solid mixture of **1** (410 mg, 0.43 mmol), $AgClO_4$ (90 mg, 0.44 mmol), and PCy_3 (362 mg, 1.29 mmol) was added MeCN (30 mL), and the resulting suspension was stirred for 18 h. An orange precipitate gradually formed, which was separated by filtration and dissolved in CH_2Cl_2 (20 mL). The turbid red solution was filtered through Celite to remove insoluble impurities and concentrated (10 mL). The addition of MeCN (40 mL) led to the precipitation of a yellow solid, which was filtered off, washed with MeCN (2 × 5 mL), and vacuum-dried to give **7c**. Yield: 563 mg, 93%. Anal. Calcd for $C_{80}H_{114}AgCuP_2S_3$: C, 68.37; H, 8.18; S, 6.84. Found: C, 68.18; H, 8.49; S, 6.57. Mp: 150 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1515, 1483, 1448. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.73, 9.36, 8.52, 8.31 (all d, $^4J_{HH} = 1.6$ Hz, 1 H each, H1, H8), 7.64, 7.63, 7.53, 7.42 (all d, $^3J_{HH} = 8.0$ Hz, 1 H each, H4, H5), 7.30, 7.24, 7.19, 7.09 (all dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.6$ Hz, 1 H each, H3, H6), 1.89−1.45 (br m, 42 H, Cy), 1.43, 1.38, 1.31 (all s, 9 H each, *t*-Bu), 1.25−0.95 (br m, 24 H, Cy), 0.79 (s, 9 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 159.4, 159.3 (br, CS_2), 149.7, 148.8, 148.2, 148.1 (C2, C7), 141.1, 140.2, 139.5, 139.0 (C8a, C9a), 137.6, 136.1, 135.6, 135.4 (C4a, C4b), 132.7, 127.9 (br, C9), 124.5, 124.2, 123.7, 123.3, 123.2, 121.5, 121.0 (C1, C8, C3, C6), 117.9, 117.6, 117.4, 117.0 (C4, C5), 35.1, 35.0, 34.9, 34.6 (CMe_3), 32.0 (d, $^1J_{CP} = 15$ Hz, C1, Cy), 31.9, 31.86, 31.84, 30.94 (CMe_3), 30.91 (br, C2, C6, Cy), 30.5 (vdd, *N* = 13 Hz, C2, C6, Cy), 27.4−27.0 (m, C3, C5, Cy), 26.1, 25.7 (C4, Cy). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 39.1 (2 d, $^1J_{P\text{-}^{107}Ag} = 542$ Hz, $^1J_{P\text{-}^{109}Ag} = 626$ Hz), 20.9 (br).

[AgCu{[SC=(*t*-Bu-fy)]$_3$S}(PPh$_3$)$_2$] (9a). A solid mixture of **1** (373 mg, 0.39 mmol) and $[Ag(PPh_3)_4]ClO_4$ (497 mg, 0.40 mmol) was suspended in THF (40 mL). After stirring for 3 h, a turbid red solution was obtained, which was concentrated to dryness. The oily residue was stirred with CH_2Cl_2 (15 mL), and the resulting suspension was filtered through Celite to remove the isoluble material. The filtrate was concentrated (10 mL), MeCN (50 mL) was added, and the resulting solution was left to stand for 24 h under atmospheric conditions, whereupon complex **9a** precipitated as a black microcrystalline solid. Yield: 230 mg, 35%, based on Cu (70% in view of the equilibrium represented in Scheme 5). Anal. Calcd for $C_{102}H_{102}AgCuP_2S_4$: C, 72.51; H, 6.09; S, 7.59. Found: C, 72.39; H, 6.26; S, 7.56. Mp: 192 °C (dec). IR (KBr, cm^{-1}): ν(C=CS_2), 1499, 1475. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.37, 8.66, 8.51 (all d, $^4J_{HH}$ = 1.6 Hz, 2 H each, H1, H8), 7.64, 7.63 (both d, $^3J_{HH}$ =8.0 Hz, 2 H each, H4, H5), 7.25, 7.20 (both dd, $^3J_{HH}$ =8.0 Hz, $^4J_{HH}$ = 1.6 Hz, 2 H each, H3, H6), 7.18−7.10 (m, 6 H, H4, H5, H3, H6 + Ph), 7.04−6.91 (m, 20 H, Ph), 6.71−6.64 (m, 6 H, Ph), 1.34, 1.11, 0.90 (all s, 18 H each, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 153.6 (dd, $^3J_{CP}$ = 8.1, 3.0 Hz, CS_2), 150.2, 148.9, 148.6 (C2, C7), 140.6 (C8a, C9a), 139.31, 139.29 (C8a, C9a, CS_2), 139.1 (C8a, C9a), 136.6, 136.4, 136.0 (C4a, C4b), 133.4 (br d, $^2J_{CP}$ = 16.2 Hz, *o*-C, PPh_3), 133.3 (d, $^2J_{CP}$ = 13.2 Hz, *o*-C, PPh_3), 132.2 (d, $^1J_{CP}$ = 31 Hz, *i*-C, PPh_3), 131.0 (br d, $^1J_{CP}$ = 33 Hz, *i*-C, PPh_3), 130.3 (t, $^4J_{CP}$ = 2.1 Hz, C9), 129.9, 129.2 (br, *p*-C, PPh_3), 128.5 (br d, $^3J_{CP}$ = 10.3 Hz, *m*-C, PPh_3), 128.2 (d, $^3J_{CP}$ = 9.2 Hz, *m*-C, PPh_3), 127.0 (C9), 125.2, 124.6, 124.5, 123.7, 122.2 (C1, C8, C3, C6), 118.4, 118.0, 117.3 (C4, C5), 35.0, 34.9, 34.8 (*C*Me_3), 31.8, 31.7, 31.0 (C*Me_3*). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 13.6 (2 d, $^1J_{P\text{-}^{107}Ag}$ = 541 Hz, $^1J_{P\text{-}^{109}Ag}$ = 623 Hz), 1.8 (s).

[AgCu{[SC=(*t*-Bu-fy)]$_3$S}(PTo$_3$)$_2$] (9b). To a solid mixture of **1** (268 mg, 0.28 mmol), $AgClO_4$ (59 mg, 0.28 mmol), and PTo_3 (261 mg, 0.86 mmol) was added THF (20 mL), and the resulting dark brown solution was stirred for 3 h. The color gradually changed to dark red. The solvent was evaporated to dryness, the oily residue was stirred with CH_2Cl_2 (15 mL), and the resulting suspension was filtered through Celite to remove the insoluble material. Partial evaporation of the clear reddish brown filtrate (5 mL) and addition of MeCN (45 mL) led to the precipitation of a purplish black microcrystalline solid, which was fitered off, washed with MeCN (2 × 2 mL), and vacuum dried to give **9b**. Yield: 130 mg, 26%, based on Cu (52% in view of the equilibrium represented in Scheme 5). Anal. Calcd for $C_{108}H_{114}AgCuP_2S_4$: C, 73.13; H, 6.48; S, 7.23. Found: C, 72.95; H, 6.40; S, 7.08. Mp: 188 °C (dec). IR (KBr, cm^{-1}): ν(C=CS_2), 1497, 1474. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.38, 8.67, 8.43 (all d, $^4J_{HH}$ = 1.6 Hz, 2 H each, H1, H8), 7.65, 7.63 (both d, $^3J_{HH}$ = 8.0 Hz, 2 H each, H4, H5), 7.24, 7.20, 7.11 (all dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H each, H3, H6), 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, H4, H5), 6.95−6.83 (m, 12 H, To), 6.75, 6.46 (both br d, $^3J_{HH}$ = 6.8 Hz, 6 H each, To), 2.22, 2.08 (both s, 9 H each, Me), 1.34, 1.09, 0.90 (all s, 18 H each, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 154.5 (dd, $^3J_{CP}$ = 11.2, 3.9 Hz, CS_2), 149.9, 148.9, 148.6 (C2, C7), 140.7 (C8a, C9a), 139.8 (br, *p*-C, To), 139.23, 139.16, 139.14 (C8a, C9a, CS_2), 138.9 (d, $^3J_{CP}$ = 1.7 Hz, *p*-C, To), 136.6, 136.3, 136.0 (C4a, C4b), 133.4 (br d, $^2J_{CP}$ = 16.5 Hz, *o*-C + *i*-C, To), 133.2 (d, $^2J_{CP}$ = 13.5 Hz, *o*-C, To), 130.0 (t, $^4J_{CP}$ = 2.0 Hz, C9), 129.3 (d, $^3J_{CP}$ = 11.4 Hz, *m*-C, To), 128.8 (d, $^3J_{CP}$ = 9.6 Hz, *m*-C, To), 128.2 (br d, $^1J_{CP}$ = 34.8 Hz, *i*-C, To), 127.1 (C9), 125.0, 124.5 (C1, C8), 124.3 (C3, C6), 123.7 (C1, C8), 122.1, 122.0 (C3, C6), 118.2, 117.9, 117.2 (C4, C5), 35.0, 34.8, 34.7 (*C*Me_3), 31.8, 31.6, 31.0 (C*Me_3*), 24.4, 21.2 (Me, To). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 11.6 (2 d, $^1J_{P\text{-}^{107}Ag}$ = 545 Hz, $^1J_{P\text{-}^{109}Ag}$ = 633 Hz), 0.2 (br).

Scheme 2[a]



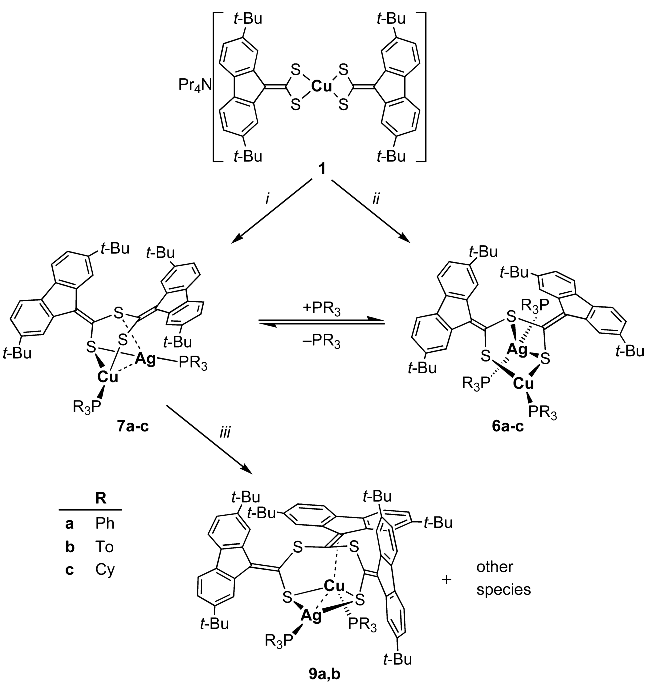
[a] (*i*) $[Cu(PPh_3)_4]ClO_4$ − $SPPh_3$ − PPh_3 − $Pr_4N(ClO_4)$ or $[Cu(NCMe)_4]PF_6$ + 3PTo_3 − $SPTo_3$ − $Pr_4N(PF_6)$. (*ii*) $[Cu(PTo_3)_4]ClO_4$ − $SPTo_3$ − $Pr_4N(ClO_4)$. To = *p*-tolyl.

Results and Discussion

Synthesis of Dicopper(I) Complexes. The reaction of the Cu(III) complex $Pr_4N[Cu\{S_2C{=}(t\text{-Bu-fy})\}_2]$ (**1**) with $[Cu(PPh_3)_4]ClO_4$ in 1:1 molar ratio in MeCN at room temperature led to the formation of the dinuclear Cu(I) complex $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PPh_3)_2]$ (**2a**) after 24 h, which was isolated in 89% yield as an orange precipitate (Scheme 2). The other products of this reaction were $Pr_4N(ClO_4)$, $SPPh_3$, and free PPh_3, which were identified in the mother liquor. We have reported the synthesis of **2a** by reacting $[Cu\{S_2C(t\text{-Bu-Hfy})\}(PPh_3)_2]$ with Et_3N under atmospheric conditions or with *p*-benzoquinone, but in lower yields (67 or 73%, respectively).[9] Curiously, the synthesis of the analogous PTo_3 complex **2b** (To = *p*-tolyl) was not fulfilled using the same procedure. Thus, the reaction of **1** with $[Cu(PTo_3)_4]ClO_4$ in 1:1 molar ratio in MeCN gave the tris(phosphine) complex $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PTo_3)_3]$ (**3b**) as an orange precipitate. Although its $^{31}P\{^1H\}$ NMR spectrum at low temperature shows that **3b** is in equilibrium with the bis(phosphine) derivative **2b** and free PTo_3 in solution (Scheme 2), pure **2b** could not be obtained through successive recrystallizations of **3b** from CH_2Cl_2/MeCN. However, the reaction of **3b** with elemental sulfur causes the displacement of the equilibrium to the formation of S=PTo_3 and **2b** (Scheme 2), which can be isolated in 71% yield.

We also carried out several attempts to directly obtain complex **2b** by reacting **1** with $[Cu(NCMe)_4]PF_6$ and PTo_3 in 1:1:3 molar ratio. When this reaction was carried out in THF, a red solution was obtained, from which the dithiolato complex $[Cu_4\{S_2C{=}(t\text{-Bu-fy})\}_2(PTo_3)_4]$[9] (**4b**) (16% yield, based on Cu) and crude **2b** (~54% yield) were successively isolated by precipitation with MeOH. However, the latter was contaminated with small amounts of decomposition

Scheme 3[a]



[a] (*i*) $AgClO_4 + 3\ PR_3 - SPR_3 - Pr_4N(ClO_4)$; (*ii*) $AgClO_4 + 4\ PR_3 - SPR_3 - Pr_4N(ClO_4)$. (*iii*) CH_2Cl_2/MeCN. To = *p*-tolyl.

products that could not be separated. By using MeCN as the precipitating agent instead of MeOH, a green precipitate was obtained, which contained **4b** and the new ligand **IV** complex $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_3S\}(PTo_3)_2]$ (**5b**). These two compounds slowly react with each other in $CDCl_3$ solution to give **2b** (see the NMR section). When the reaction of **1** with $[Cu(NCMe)_4]PF_6$ and PTo_3 in 1:1:3 molar ratio was carried out in MeCN, a mixture of **3b**, **4b**, and **5b** was obtained as an ochre precipitate. Purplish black crystals of **5b** can be obtained when suspensions of **2b** in MeCN are allowed to stand for several days. However, the isolated amounts of **5b** were not enough for a complete characterization, and the crystals were not suitable for X-ray single crystal studies. Its ^1H and $^{31}P\{^1H\}$ NMR data are consistent with its formulation as an analogue of the heterodinuclear complexes $[AgCu\{[SC{=}(t\text{-Bu-fy})]_3S\}(PR_3)_2]$ [R = Ph (**9a**), To (**9b**)], whose preparation is described in the next section.

Synthesis of Silver(I)/Copper(I) Complexes. By reacting **1** with $AgClO_4$ and PR_3 in 1:1:4 molar ratio in MeCN, complexes $[AgCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_3]$ [R = Ph (**6a**), *p*-To (**6b**), PCy_3 (**6c**)] were obtained in high yields as yellow (**6a**) or orange (**6b** and **c**) precipitates (Scheme 3). When the reaction of **1** with $AgClO_4$ and PCy_3 was carried out in 1:1:3 molar ratio, a high yield of the complex $[AgCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**7c**) was obtained. The only other products of the above reactions were $Pr_4N(ClO_4)$ and the corresponding $S{=}PR_3$, which were identified by NMR spectroscopy. Complex **6c** is in equilibrium with **7c** and free PCy_3 in solution. In addition, small amounts of $[Cu_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**2c**), which has been previously reported by us,[9] and the non-isolated disilver derivative $[Ag_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PCy_3)_2]$ (**8c**; see NMR discussion and Scheme 6) are observed in solutions of **6c** or **7c**.

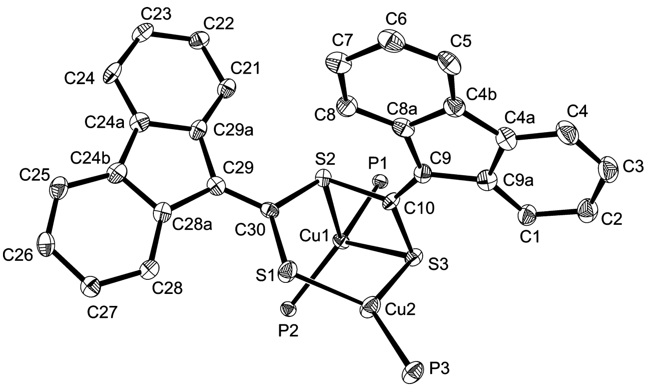


Figure 1. Thermal ellipsoid plot (50 % probablility) of complex **3b**. H atoms and *t*-Bu and To groups have been omitted for clarity.

The PPh_3 and PTo_3 derivatives **6a** and **b** are considerably less stable in solution than the PCy_3 complex **6c**, and they establish a series of equilibria in solution leading to the formation of limited amounts of the dicopper complexes **2a** or **3b**, their disilver homologues, $[Ag_2\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_2]$ [R = Ph (**8a**), To (**8b**); see NMR Section], and the heterodinuclear complexes $[CuAg\{[SC{=}(t\text{-Bu-fy})]_3S\}(PR_3)_2]$ [R = Ph (**9a**), To (**9b**)], containing ligand **IV** (Scheme 3). Other species observed could not be identified. Complexes **9a**,**b** were isolated in the unsuccessful attempts to prepare the heterodinuclear complexes **7a,b**. Thus, the reactions of **1** with $AgClO_4$ and PPh_3 or PTo_3 in 1:1:3 molar ratio in MeCN gave greenish brown precipitates from which complexes **9a** or **b** can be extracted with CH_2Cl_2. The other products of these reactions are $S{=}PR_3$, $Pr_4N(ClO_4)$, and unidentified insoluble materials. Better yields in **9a**,**b** were obtained using THF as solvent (35% and 26%, respectively, based on Cu). The PPh_3 derivative **9a** can be also prepared by using $[Ag(PPh_3)_4]ClO_4$ as the silver precursor or by successive recrystallizations of complex **6a** from CH_2Cl_2/MeCN.

Crystal Structures of Complexes. The X-ray diffraction structure of complex **2a** has been previously reported by us.[9] The condensed dithiolato ligand **III** binds one of the $[Cu(PPh_3)]^+$ units through the terminal sulfur atoms and the other through the $C{=}CS_2$ double bond of a fluoren-9-ylidene group and one of the terminal sulfur atoms. (Scheme 2). The PTo_3 analogue **2b** is expected to present a similar structure, although this could not be confirmed by means of X-ray diffraction studies.

The X-ray single-crystal structure analyses of the homodinuclear Cu(I) complex **3b** and the heterodinuclear Cu(I)/Ag(I) complex **6b** revealed that these complexes are nearly isostructural. Different perspective views of their crystal structures are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Tables 2 and 3. In both cases, the condensed ligand **III** is coordinated to a $[Cu(PTo_3)]^+$ unit through both terminal sulfur atoms and to a $[M(PTo_3)_2]^+$ unit [M = Cu (**3b**), Ag (**6b**)] through one of the terminal sulfur atoms and the central one. The conformation of the condensed ligand is almost identical for both structures, the two S−C−S planes forming an angle of 91.13° (**3b**) or 89.02° (**6b**). The fluoren-9-ylidene fragments are nearly planar, with their respective mean planes slightly

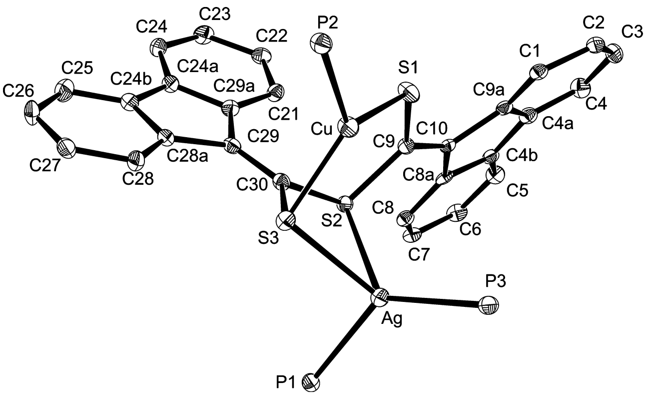


Figure 2. Thermal ellipsoid plot (50 % probablility) of complex **6b**. H atoms and *t*-Bu and To groups have been omitted for clarity.

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

Cu(1)−P(2)	2.2605(11)	S(1)−C(30)	1.714(4)
Cu(1)−P(1)	2.2931(11)	S(2)−C(10)	1.792(4)
Cu(1)−S(3)	2.3704(11)	S(2)−C(30)	1.807(4)
Cu(1)−S(2)	2.5625(11)	S(3)−C(10)	1.774(4)
Cu(2)−P(3)	2.1951(13)	C(9)−C(10)	1.364(6)
Cu(2)−S(1)	2.2075(12)	C(29)−C(30)	1.372(6)
Cu(2)−S(3)	2.2599(12)		
P(2)−Cu(1)−P(1)	127.98(4)	C(30)−S(1)−Cu(2)	111.79(14)
P(2)−Cu(1)−S(3)	118.95(4)	C(10)−S(2)−C(30)	107.58(19)
P(1)−Cu(1)−S(3)	100.19(4)	C(10)−S(2)−Cu(1)	84.36(13)
P(2)−Cu(1)−S(2)	123.98(4)	C(30)−S(2)−Cu(1)	108.04(13)
P(1)−Cu(1)−S(2)	98.31(4)	C(10)−S(3)−Cu(2)	79.37(14)
S(3)−Cu(1)−S(2)	72.89(4)	C(10)−S(3)−Cu(1)	90.74(14)
P(3)−Cu(2)−S(1)	113.56(5)	Cu(2)−S(3)−Cu(1)	101.51(4)
P(3)−Cu(2)−S(3)	125.36(5)	S(3)−C(10)−S(2)	110.8(2)
S(1)−Cu(2)−S(3)	117.39(4)	S(1)−C(30)−S(2)	118.2(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **6b**

Ag(1)−P(3)	2.4034(8)	S(1)−C(10)	1.727(3)
Ag(1)−P(1)	2.4689(7)	S(2)−C(10)	1.798(3)
Ag(1)−S(3)	2.5717(7)	S(2)−C(30)	1.798(3)
Ag(1)−S(2)	2.7921(7)	S(3)−C(30)	1.767(3)
Cu(1)−P(2)	2.1981(8)	C(9)−C(10)	1.377(4)
Cu(1)−S(1)	2.2124(8)	C(29)−C(30)	1.361(4)
Cu(1)−S(3)	2.2587(8)		
P(3)−Ag(1)−P(1)	130.71(3)	C(10)−S(1)−Cu(1)	111.82(10)
P(3)−Ag(1)−S(3)	121.35(2)	C(10)−S(2)−C(30)	108.28(13)
P(1)−Ag(1)−S(3)	97.84(2)	C(10)−S(2)−Ag(1)	103.38(9)
P(3)−Ag(1)−S(2)	125.58(2)	C(30)−S(2)−Ag(1)	85.38(9)
P(1)−Ag(1)−S(2)	95.13(2)	C(30)−S(3)−Cu(1)	81.21(9)
S(3)−Ag(1)−S(2)	67.34(2)	C(30)−S(3)−Ag(1)	93.05(9)
P(2)−Cu(1)−S(1)	113.82(3)	Cu(1)−S(3)−Ag(1)	98.55(3)
P(2)−Cu(1)−S(3)	124.02(3)	S(1)−C(10)−S(2)	118.45(16)
S(1)−Cu(1)−S(3)	117.22(3)	S(3)−C(30)−S(2)	113.33(15)

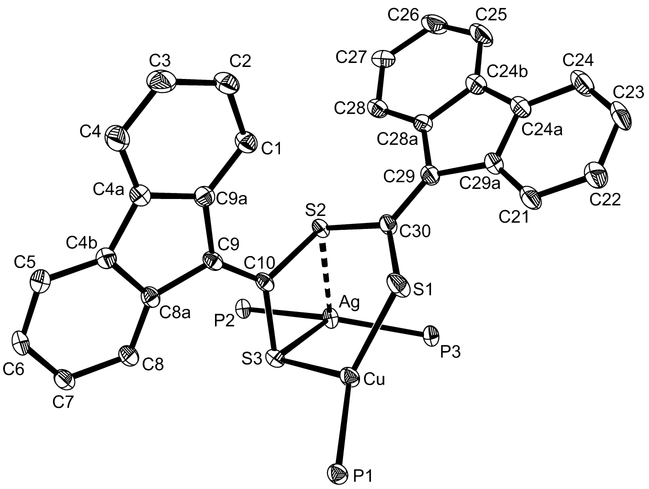


Figure 3. Thermal ellipsoid plot (50 % probablility) of complex **6c**. H atoms and *t*-Bu and Cy groups have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **6c**

Ag(1)−P(3)	2.4182(6)	S(1)−C(30)	1.731(2)
Ag(1)−P(2)	2.4673(5)	S(2)−C(10)	1.791(2)
Ag(1)−S(3)	2.6529(5)	S(2)−C(30)	1.792(2)
Ag(1)−S(2)	2.9282(5)	S(3)−C(10)	1.751(2)
Cu(1)−S(1)	2.2028(6)	C(9)−C(10)	1.363(3)
Cu(1)−P(1)	2.2086(6)	C(29)−C(30)	1.382(3)
Cu(1)−S(3)	2.2624(6)		
P(3)−Ag(1)−P(2)	136.359(19)	P(1)−Cu(1)−S(3)	114.72(2)
P(3)−Ag(1)−S(3)	122.669(18)	C(30)−S(1)−Cu(1)	113.29(7)
P(2)−Ag(1)−S(3)	95.461(17)	C(10)−S(2)−C(30)	107.77(9)
P(3)−Ag(1)−S(2)	109.197(17)	C(10)−S(3)−Cu(1)	88.40(7)
P(2)−Ag(1)−S(2)	106.186(17)	C(10)−S(3)−Ag(1)	92.76(7)
S(3)−Ag(1)−S(2)	63.974(15)	Cu(1)−S(3)−Ag(1)	108.59(2)
S(1)−Cu(1)−P(1)	127.42(2)	S(3)−C(10)−S(2)	113.72(11)
S(1)−Cu(1)−S(3)	112.66(2)	S(1)−C(30)−S(2)	118.39(11)

rotated with respect to the corresponding S−C−S planes and forming an angle of 73.41° (**3b**) or 72.03° (**6b**) with each other. The tricoordinated Cu atoms in both structures are in slightly distorted trigonal planar environments, with very similar Cu−S distances (range 2.21−2.26 Å). The tetracoordinated Cu or Ag atoms are in highly distorted tetrahedral environments, mainly because of the small bite of the CS_2 moiety and the different M−S distances. The Cu(1)−S(2) distance in **3b** [2.5625(11) Å] is appreciably longer than Cu(1)−S(3) [2.3704(11) Å], which is attributable to the expected lower coordination ability of the central S(2) atom, and both are significantly longer than for the trigonal Cu(2) center. Analogously, in the case of **6b**, the Ag−S(1) distance [2.5717(7) Å] is normal, while the Ag−S(2) distance [2.7921(7) Å] is much longer. The distances between the two metal centers [3.587 Å (**3b**), 3.666 (**6b**)] are too long to consider metallophilic interactions.

The crystal structures of the PCy_3 complexes **6c** (Figure 3, Table 4) and **7c** (Figure 4, Table 5) were solved as CH_2Cl_2 or CH_2Cl_2/MeCN solvates, respectively. In both cases the condensed ligand **III** is coordinated to a $[Cu(PCy_3)]^+$ unit through both terminal sulfur atoms, and to a $[Ag(PCy_3)_2]^+$

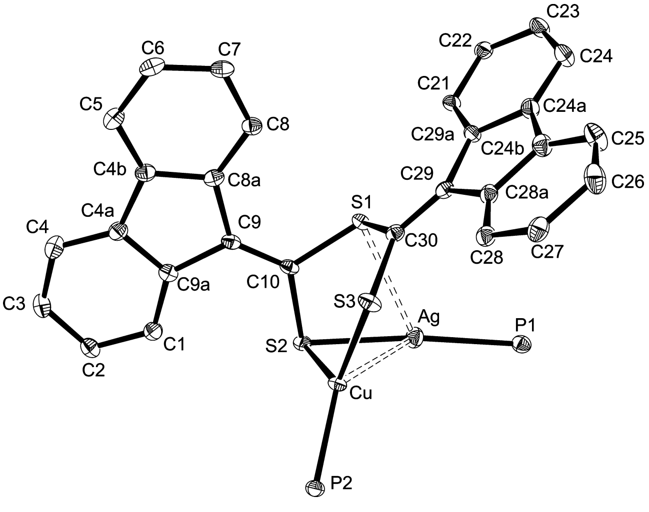


Figure 4. Thermal ellipsoid plot (50 % probablility) of complex **7c**. H atoms and *t*-Bu and Cy groups have been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **7c**

Ag(1)−P(1)	2.3407(7)	S(1)−C(10)	1.789(2)
Ag(1)−S(2)	2.4052(7)	S(1)−C(30)	1.799(3)
Ag(1)−Cu(2)	2.8157(4)	S(2)−C(10)	1.781(3)
Ag(1)−S(1)	2.8610(7)	S(3)−C(30)	1.734(3)
Cu(2)−P(2)	2.2191(7)	C(9)−C(10)	1.355(4)
Cu(2)−S(3)	2.2202(7)	C(29)−C(30)	1.372(3)
Cu(2)−S(2)	2.2946(7)		
P(1)−Ag(1)−S(2)	171.67(2)	C(30)−S(1)−Ag(1)	89.97(8)
P(1)−Ag(1)−S(1)	119.55(2)	C(10)−S(2)−Cu(2)	91.09(8)
S(2)−Ag(1)−S(1)	68.15(2)	C(10)−S(2)−Ag(1)	96.67(8)
P(2)−Cu(2)−S(3)	124.13(3)	Cu(2)−S(2)−Ag(1)	73.57(2)
P(2)−Cu(2)−S(2)	122.28(3)	C(30)−S(3)−Cu(2)	113.25(9)
S(3)−Cu(2)−S(2)	111.19(3)	S(2)−C(10)−S(1)	112.88(14)
C(10)−S(1)−C(30)	107.38(11)	S(3)−C(30)−S(1)	118.44(14)
C(10)−S(1)−Ag(1)	81.95(8)		

(**6c**) or a $[Ag(PCy_3)]^+$ (**7c**) unit through one of them, while the central S atom establishes weaker interactions with the Ag atoms. The conformations found for the ligand are slightly more open than that observed for **3b** and **6b**, with the two S−C−S planes forming an angle of 86.24° (**6c**) or 93.49° (**7c**). The Cu atoms are in slightly distorted trigonal planar environments, and the Cu−S distances are similar to the corresponding distances found for **3b** and **6b**. The coordination environment of the Ag atom in **6c** is appreciably different to that found for the PTo_3 complex **6b**, being best described as trigonal planar (main deviation from the Ag, P(2), P(3) and S(3) plane, 0.141 Å) with some degree of distortion toward the tetrahedral geometry because of the weak interaction with the central S(2) atom [Ag−S(2): 2.9282(5) Å, Ag−S(1): 2.6529(5) Å]. The observed differences between **6b** and **6c** are probably a consequence of the greater steric hindrance of the PCy_3 ligand as compared to PTo_3. The coordination environment for the Ag atom in **7c** is practically linear, with a relatively short Ag−S(2) distance of 2.4052(7) Å and a S(2)−Ag–P(1) angle of 171.67(2)°, while the Ag−S(1) distance of 2.8610(7) Å is very long and can be considered as a secondary, much weaker interaction. The Cu−Ag distance in **6c** [3.998 Å] is even longer than that found for **3b** and **6b**, while for **7c** [2.8157(4) Å] it is shorter than the sum of the van der Waals radii for these metals (3.12 Å),[16] indicating the presence of a metallophilic interaction.

The condensed ligand **IV** in complex **9a** (Figure 5, Table 6) adopts a conformation in which consecutive fluoren-9-ylidene fragments arrange almost perpendicularly to each other, the mean planes of the terminal fluoren-9-ylidene fragments forming angles of 88.91° and 91.63° with that of the central one. The ligand employs the terminal sulfur atoms S(1) and S(4) to bridge the $[Ag(PPh_3)]^+$ and $[Cu(PPh_3)]^+$ units and, additionally, the C(9)═C(10) double bond of the central fluoren-9-ylidene group is coordinated to the Cu atom. The resulting coordination environments are distorted trigonal planar for Ag and distorted tetrahedral for Cu. Considering the C(9)═C(10) bond centroid, the angles around the Cu atom are close to the ideal value for the tetrahedral geometry, except for the centroid−Cu−P(1) angle (134.89°). The Cu−S and Ag−S distances are comparable to the corresponding

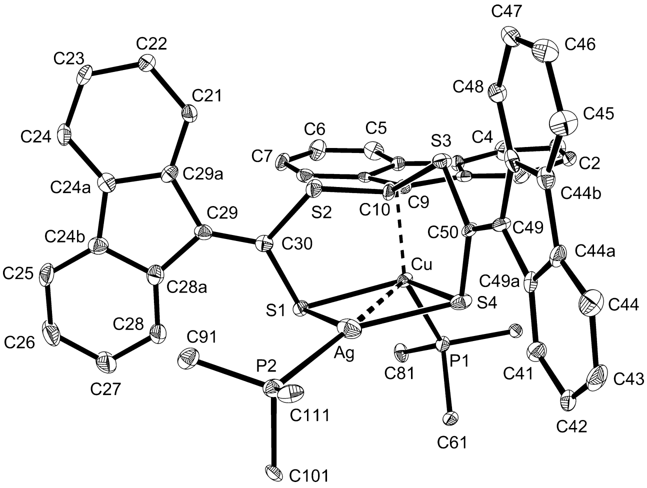


Figure 5. Thermal ellipsoid plot (50 % probablility) of complex **9a**. H atoms and *t*-Bu and Ph groups have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **9a**

Ag(1)−P(2)	2.3617(12)	S(1)−C(30)	1.759(4)
Ag(1)−S(4)	2.4747(12)	S(2)−C(10)	1.785(4)
Ag(1)−S(1)	2.6997(11)	S(2)−C(30)	1.789(4)
Ag(1)−Cu(1)	2.9606(6)	S(3)−C(50)	1.781(4)
Cu(1)−C(10)	2.088(4)	S(3)−C(10)	1.798(4)
Cu(1)−C(9)	2.208(4)	S(4)−C(50)	1.757(4)
Cu(1)−P(1)	2.2677(11)	C(9)−C(10)	1.404(6)
Cu(1)−S(4)	2.2960(12)	C(29)−C(30)	1.350(6)
Cu(1)−S(1)	2.3989(12)	C(49)−C(50)	1.366(5)
P(2)−Ag(1)−S(4)	147.77(4)	C(30)−S(1)−Cu(1)	102.87(14)
P(2)−Ag(1)−S(1)	110.66(4)	C(30)−S(1)−Ag(1)	87.62(14)
S(4)−Ag(1)−S(1)	98.66(3)	Cu(1)−S(1)−Ag(1)	70.71(3)
C(10)−Cu(1)−P(1)	153.68(12)	C(10)−S(2)−C(30)	111.05(18)
C(9)−Cu(1)−P(1)	116.79(11)	C(50)−S(3)−C(10)	104.67(19)
C(10)−Cu(1)−S(4)	88.71(11)	C(50)−S(4)−Cu(1)	108.06(14)
C(9)−Cu(1)−S(4)	115.48(11)	C(50)−S(4)−Ag(1)	98.09(14)
P(1)−Cu(1)−S(4)	102.41(4)	Cu(1)−S(4)−Ag(1)	76.62(4)
C(10)−Cu(1)−S(1)	93.63(11)	S(2)−C(10)−S(3)	103.4(2)
C(9)−Cu(1)−S(1)	104.95(11)	S(1)−C(30)−S(2)	114.5(2)
P(1)−Cu(1)−S(1)	103.31(4)	S(4)−C(50)−S(3)	115.6(2)
S(4)−Cu(1)−S(1)	113.53(4)		

M−S distances involving bridging S atoms in the structures of **2a**,[9] **3c**, **6b**, or **7c**. The distance of the Cu atom to the C(9)═C(10) bond centroid of 2.031 Å is sligthly shorter than the corresponding distance found for **2a** (2.056 Å). As expected, the C(9)═C(10) bond [1.404(6) Å], which is coordinated to Cu, is longer than the uncoordinated C(29)═C(30) and C(49)═C(50) bonds [1.350(6) and 1.366(5) Å, respectively]. The two metal centers establish a metallophilic contact of 2.9606(6) Å, which is slightly longer than that found for **7c**. We note that only fourteen crystal

---

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(17) (a) Wei, Q. H.; Yin, G. Q.; Zhang, L. Y.; Chen, Z. N. *Organometallics* **2006**, *25*, 4941–4944. (b) Seewald, O.; Florke, U.; Egold, H.; Haupt, H. J.; Schwefer, M. *Z. Anorg. Allg. Chem.* **2006**, *632*, 204–210. (c) Pattacini, R.; Barbieri, L.; Stercoli, A.; Cauzzi, D.; Graiff, C.; Lanfranchi, M.; Tiripicchio, A.; Elviri, L. *J. Am. Chem. Soc.* **2006**, *128*, 866–876. (d) Wei, Q. H.; Yin, G. Q.; Zhang, L. Y.; Shi, L. X.; Mao, Z. W.; Chen, Z. N. *Inorg. Chem.* **2004**, *43*, 3484–3491. (e) Shorrock, C. J.; Xue, B. Y.; Kim, P. B.; Batchelor, R. J.; Patrick, B. O.; Leznoff, D. B. *Inorg. Chem.* **2002**, *41*, 6743–6753. (f) Fackler, J. P.; Lopez, C. A.; Staples, R. J.; Wang, S. N.; Winpenny, R. E. P.; Lattimer, R. P. *J. Chem. Soc., Chem. Commun.* **1992**, 146–148. (g) Abu-Salah, O. M.; Hussain, M. S.; Schlemper, E. O. *J. Chem. Soc., Chem. Commun.* **1988**, 212–213. (h) Freeman, M. J.; Orpen, A. G.; Salter, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1001–1008. (i) Freeman, M. J.; Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1332–1334.

Table 7. ^{1}H NMR Resonances of the H1/H8 Atoms for the Complexes Mentioned in This Work[a]

compd	δ(H1/H8)
2a	9.64, 8.66
2b	9.58, 8.61
2c	9.61, 8.55
3b	9.58, 8.58 (298 K) 10.22, 9.10, 8.56, 8.40 (213 K)
4b	9.41
5b	9.28, 8.57, 8.34
6a	9.81, 9.43, 8.54, 8.47
6b	9.79, 9.38, 8.47, 8.45
6c	9.90, 9.72, 8.57, 8.16
7c	9.73, 9.36, 8.52, 8.31
8a	9.77, 8.58
8b	9.74, 8.54
8c	9.68, 8.52
9a	9.37, 8.66, 8.51
9b	9.38, 8.67, 8.43

[a] ppm, $CDCl_3$ solution.

structures in the Cambridge Structural database display metallophilic Ag···Cu contacts.[17] Most of them correspond to high-nuclearity clusters, which may include other metals, and the Ag−Cu distances range from 2.575 to 3.238 Å. At the time of submission of this article, no structural data for dinuclear Ag/Cu complexes showing short metallophilic contacts had been deposited.

NMR Spectra, Phosphine Dissociation and Dynamic Behavior. The ^{1}H NMR spectra of the complexes with condensed dithiolato ligands show the resonances of the H1/H8 protons of the fluoren-9-ylidene groups (see Chart 1 for the atom numbering) at high frequencies (range 10.2−8.2 ppm; Table 7) and are useful for the identification of the different complexes in mixtures because they usually do not overlap with any other signals. Therefore, in discussing the ^{1}H NMR spectra, we will only mention the H1/H8 resonances; the H3/H6, H4/H5 and *t*-Bu signals are reported in the Experimental Section.

The dicopper complex **2b**, like its already reported analogues with PPh_3 (**2a**), PCy_3 (**2c**), and dppf,[9] gives rise to two resonances for the H1/H8 protons instead of the expected four resonances in view of the crystal structure of **2a**, which shows the two *t*-Bu-fy groups of the condensed dithiolate **III** in different environments (Scheme 2). We have proposed a dynamic process that causes the copper atoms to interchange their coordination environments, or a different, C_2-symmetrical structure of the complexes in solution.[9]

The ^{1}H NMR spectrum of **2b** in $CDCl_3$ also reveals the presence of very small amounts of the dithiolato complex **4b** and the ligand **IV** complex **5b** (Scheme 2), which give rise to one or three resonances, respectively, for the H1/H8 protons. The NMR data for **5b** are discussed below, together with those of its heterodinuclear analogues **9a** and **b**. The presence of **4b** and **5b** in solutions of **2b** suggests the existence of an equilibrium which is almost entirely displaced towards the formation of **2b** in $CDCl_3$. In fact, when the solid mixtures of **4b** and **5b**, obtained from the reaction of **1** with $[Cu(NCMe)_4]PF_6$ and PTo_3 in 1:1:3 molar ratio in MeCN, are dissolved in $CDCl_3$, the ^{1}H NMR spectra show the gradual transformation of the mixture into **2b** (Figure 6).

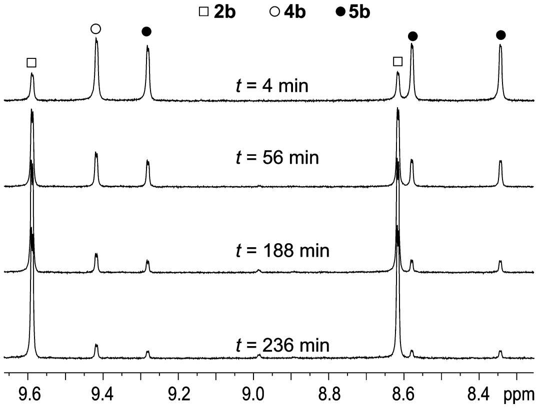


Figure 6. NMR spectra of a mixture of **4b** and **5b** (~1.2:2 molar ratio) at different times after dissolution in $CDCl_3$, showing the gradual formation of **2b** (H1 and H8 resonances).

The ^{1}H NMR spectrum of **3b** at room temperature shows two signals for the H1/H8 protons, while the resonances of the aromatic protons of the PTo_3 ligands are broad and only one signal for the Me groups of the phosphines is observed. The $^{31}P\{^1H\}$ NMR spectrum shows a very broad signal at 4.8 ppm. These data suggested the existence of exchange processes in solution, which were investigated by means of low-temperature NMR measurements. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra of **3b** at 213 K in $CDCl_3$ showed the signals corresponding to complexes **2b**, **3b**, and free PTo_3. Complex **3b** gives rise to the four expected resonances for the H1/H8 protons (10.22, 9.10, 8.56, and 8.40 ppm) due to two inequivalent *t*-Bu-fy groups, and the $[Cu(PTo_3)_2]^+$ unit gives an AB system in the $^{31}P\{^1H\}$ NMR spectrum (−0.46, −6.62 ppm; $^2J_{AB} = 117.8$ Hz), while the $[Cu(PTo_3)]^+$ unit gives a singlet at −0.33 ppm (see Supporting Information). The ratio **2b**/**3b** estimated from the integration of the H1/H8 resonances is approximately 1:3. The signals observed at room temperature are thus the result of a complex dynamic process involving the dissociation and exchange of the phosphine ligands, eventually leading to the equivalence of the *t*-Bu-fy groups.

The room temperature ^{1}H NMR spectra of complexes **6a-c** and **7c** show in the H1/H8 region the expected four resonances of the same intensity and a few others of low intensity corresponding to other complexes. In the cases of the PPh_3 or PTo_3 derivatives **6a** or **b**, the additional signals that emerge gradually are due to **2a**, **8a** and **9a** or **3b**, **8b** and **9b**, respectively, and to other unidentified species (see Supporting Information). Despite the fact that the ^{1}H NMR show well resolved signals, the $^{31}P\{^1H\}$ NMR spectra of solutions of **6a** and **b** show a very broad resonance, indicating that phosphine dissociation and exchange processes take place. In contrast, the ^{1}H and $^{31}P\{^1H\}$ NMR spectra of the PCy_3 derivatives **6c** and **7c** show only very small amounts of the dicopper and disilver complexes **2c** and **8c**, and their ^{31}P resonances resolve clearly. At 213 K, the $^{31}P\{^1H\}$ NMR spectrum of **6c** shows the resonances arising from the $[Ag(PCy_3)_2]^+$ unit as the A and B parts of two ABX systems because of the coupling of the phosphorus atoms with each other and the two isotopes of silver, while the $[Cu(PCy_3)]^+$ unit gives rise to a somewhat broad singlet (Figure 7). As

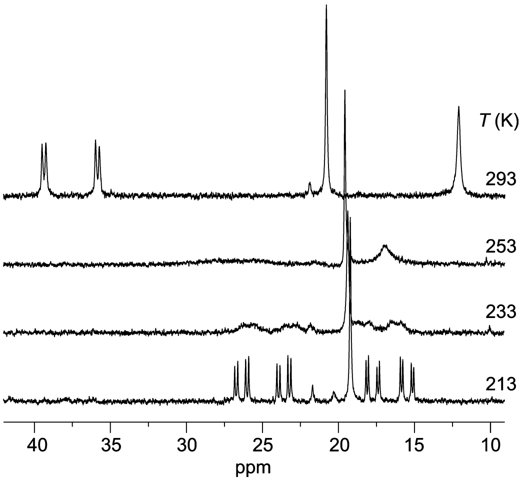


Figure 7. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of a solution of **6c** in CD_2Cl_2.

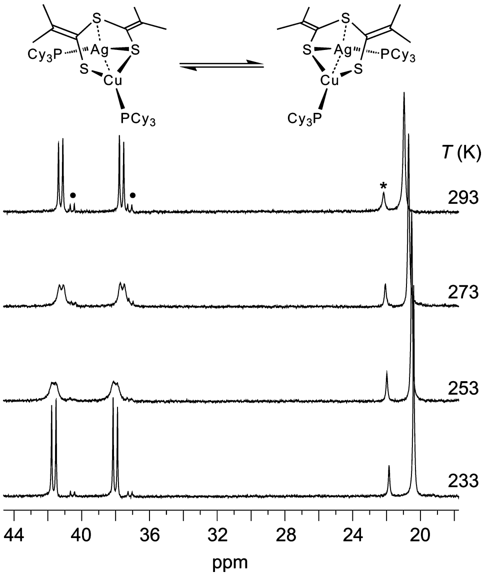


Figure 8. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of a solution of **7c** in CD_2Cl_2. The marked signals correspond to **2c** (*) and **8c** (●).

the temperature rises, the resonances of the $[Ag(PCy_3)_2]^+$ unit broaden and the $[Cu(PCy_3)]^+$ singlet shifts to higher frequencies. At room temperature, the observed signals essentially correspond to the bis(phosphine) complex **7c** and free PCy_3, suggesting a very high degree of dissociation.

The $^{31}P\{^1H\}$ NMR spectra of complex **7c** in CD_2Cl_2 at temperatures between 233 and 293 K (Figure 8) show subtle changes that affect mainly the resonance arising from the $[Ag(PCy_3)]^+$ unit, which is observed at 233 K as two doublets centered at 39.83 ppm ($^1J_{P\text{-}^{107}Ag} = 547$ Hz, $^1J_{P\text{-}^{109}Ag} = 631$ Hz), in agreement with the structure found in the solid state. As the temperature rises to 253 K, the doublets broaden and then sharpen again and shift to 39.45 ppm at room temperature. The observed changes are probably due to the migration of the $[Ag(PCy_3)]^+$ unit from one of the terminal S atoms to the other, which may involve intermediate species with different bonding environments for the Ag atom. The observation of P−Ag couplings in **7c** indicates that phosphine exchange, if it exists, is negligible, which contrasts with the solution behavior of **6c** (see above).

Since complexes **8a-c** could not be isolated, their NMR data (see Table 7 for the chemical shifts of the two H1/H8 resonances) have been taken from the ^1H NMR spectra of the solutions in which they form, namely those of **6a-c** and **7c** in $CDCl_3$ or CD_2Cl_2. In the case of the PCy_3 complex **8c**, the assignment is straightforward because it forms along with the dicopper complex **2c**[9] through the exchange of $[Ag(PCy_3)]^+$ and $[Cu(PCy_3)]^+$ units between molecules of **7c**. Moreover, the $^{31}P\{^1H\}$ NMR spectra of **6c** and **7c** in $CDCl_3$ show the resonance corresponding to the equivalent PCy_3 ligands in **8c** as two doublets centered at 38.50 ppm ($^1J_{P\text{-}^{107}Ag} = 512$ Hz, $^1J_{P\text{-}^{109}Ag} = 590$ Hz). Figure 8 shows the $^{31}P\{^1H\}$ NMR resonance of **8c** in a solution of **7c** in CD_2Cl_2, which remains unchanged between 233 and 293 K. The observed Ag−P couplings are consistent with $[Ag(PCy_3)]^+$ units that do not undergo significant phosphine dissociation. The NMR spectra of **6a** and **b** could not be used to obtain the $^{31}P\{^1H\}$ NMR data for **8a** and **b**, because of phosphine exchange processes, but their ^1H NMR data allowed us to assign the H1/H8 chemical shifts of the **8a** and **b** protons because of their similarity with those found for **8c**.

The ^1H NMR spectra of the heterodinuclear complexes **9a** and **b**, containing the condensed ligand **IV**, show the three resonances of the same intensity for the H1/H8 protons expected in view of the crystal structure of **9a**. The $^{31}P\{^1H\}$ NMR spectra show the resonance of the P atom bonded to Ag as two doublets and one singlet assignable to the P atom bonded to Cu. The ^1H NMR data of complex **5b** are very similar to those of its heteronuclear analogues **9a** and **b**. Not only do the number of aromatic signals and *t*-Bu groups match but also their chemical shifts are almost identical to those found for the PTo_3 derivative **9b**. Moreover, the $^{31}P\{^1H\}$ NMR spectrum of **5b** shows two resonances at room temperature because of two $[Cu(PTo_3)]^+$ units in different coordination environments, and one of them almost coincides with the signal assigned to the $[Cu(PR_3)]^+$ unit in **9a** and **b**. Therefore, the NMR data of **5b** indicate that this complex has essentially the same structure as its heterodinuclear derivatives **9a** and **b**.

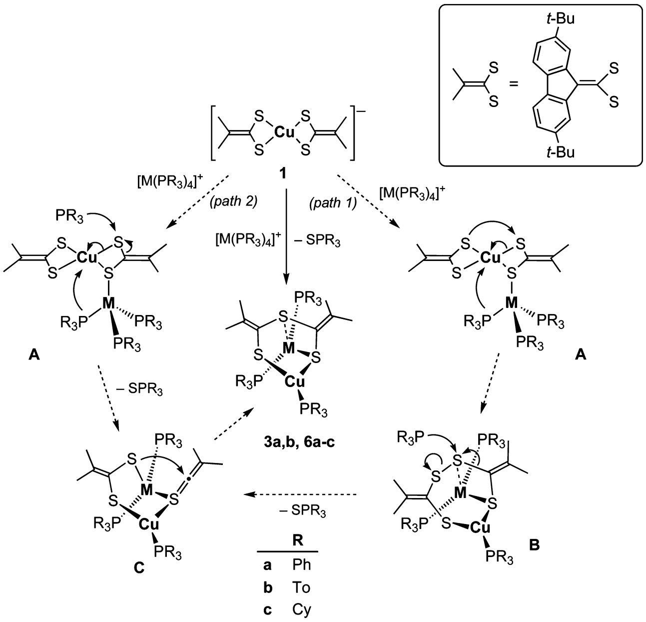
IR Spectra. The solid state IR spectra of the complexes with condensed ligand **III 2b**, **3b**, **6a-c**, and **7c** show three bands in the range 1517−1447 cm^{-1} assignable to $\nu(C{=}CS_2)$ modes[18] (see the Experimental Section). Notably, these bands coincide in energy for the isostructural complexes **3b** and **6b**. Complexes **5b**, **9a**, and **9b**, containing ligand **IV**, give rise to two bands at around 1499 and 1475 cm^{-1}; the very similar patterns and energies of the absorptions observed for these complexes also suggest that they have the same structure in the solid state.

Mechanism of Formation. The lability of Cu(I)−S and Ag(I)−S bonds is evidenced by the great variability of structures and coordination environments found in the

---

(18) Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1968**, *22*, 1107–1128.

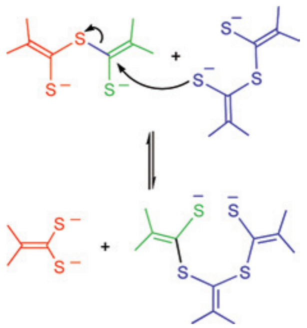
Scheme 4[a]



[a] M = Cu, Ag.

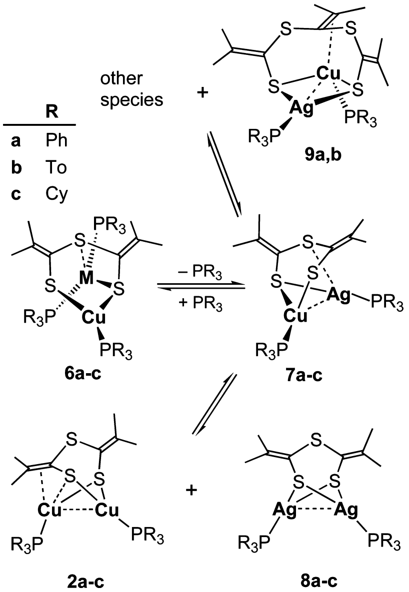
thiolato complexes of these metals[19] and the numerous cluster transformation examples reported in the literature.[20] Although it is difficult to propose a simple reaction path for the formation of the our dinuclear Cu(I) or Cu(I)/Ag(I) complexes with condensed dithiolato and phosphine ligands, some of the key steps can be rationalized from the available experimental data. The formation from **1** of the dinuclear complexes with ligand **III** involves the reduction of Cu(III) to Cu(I) and the sulfur abstraction by one of the phosphines to give phosphine sulfide. Since complex **1** is not reduced by free phosphines, it is reasonable to assume that the dithiolate condensation is triggered by the coordination of one of the sulfur atoms of **1** to Cu(I) or Ag(I) (Scheme 4) with the concomitant displacement of one of the phosphine ligands of the precursor $[M(PR_3)_4]^+$. This should weaken the stabilizing effect of the π donation of the sulfur atoms on the Cu(III) center, making it more susceptible to reduction. The reduction of the Cu(III) center could take place through the reductive elimination of two of the thiolate functions to form a disulfide-bridged dinuclear Cu(I) intermediate such as **B** (Scheme 4, path 1), which would then undergo sulfur abstraction by the displaced phosphine. Tetraalkylthiuram disulfides $R_2NC(S)SSC(S)NR_2$ have been reported to undergo a similar reaction when treated with Cu(I) halides in the presence of PPh_3, which leads to the formation of complexes containing the corresponding monosulfide $R_2NC(S)SC(S)NR_2$.[21] An alternative reduction process could involve the direct attack of a phosphine to one of the sulfur atoms of the dithiolato ligand (Scheme 4, path 2). In either case, the condensed ligand **III** in **3b** and **6a-c** presumably results from the nucleophillic attack of a dithiolate to the thioketene compound (2,7-di-*tert*-butylfluoren-9-ylidene)methanethione (**V**, Chart 1), which may exist as a coordinated ligand (intermediate **C**) or as short-lived free species after the sulfur abstraction.[22] As demonstrated for **3b** and **6c**, these complexes are in equilibrium with the corresponding bis(phosphine) derivatives **2b** and **7c** and free phosphine in solution. Probably, the greater tendency to dissociate phosphine of **3a** as compared to **3b** leads to the isolation of complex **2a** instead of **3a**.

Scheme 5[a]



[a] *t*-Bu-fy groups have been omitted.

Scheme 6[a]



[a] *t*-Bu-fy groups have been omitted.

As mentioned in the Synthesis of Dicopper Complexes and NMR Sections, complex **2b** is in equilibrium with **4b** and **5b** in solution (Scheme 2). This equilibrium is represented in Scheme 5 as the reaction between two ligands **III** (as those present in **2b**) to give a dithiolate and ligand **IV**

---

(19) (a) Su, W. P.; Hong, M. C.; Weng, J. B.; Liang, Y. C.; Zhao, Y. J.; Cao, R.; Zhou, Z. Y.; Chan, A. S. C. *Inorg. Chim. Acta* **2002**, *331*, 8–15. (b) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121. (c) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(20) (a) Coucouvanis, D.; Kanodia, S.; Swenson, D.; Chen, S. J.; Studemann, T.; Baenziger, N. C.; Pedelty, R.; Chu, M. *J. Am. Chem. Soc.* **1993**, *115*, 11271–11278. (b) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Pedelty, R.; Caffery, M. L.; Kanodia, S. *Inorg. Chem.* **1989**, *28*, 2829–2836. (c) Fackler, J. P.; Staples, R. J.; Liu, C. W.; Stubbs, R. T.; Lopez, C.; Pitts, J. T. *Pure Appl. Chem.* **1998**, *70*, 839–844. (d) Liu, C. W.; Staples, R. J.; Fackler, J. P *Coord. Chem. Rev.* **1998**, *174*, 147–177. (e) Kanodia, S.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 469–475.

(21) Victoriano, L. I.; Garland, M. T.; Vega, A.; López, C. *J. Chem. Soc., Dalton Trans.* **1998**, 1127–1132.

(present in **4b** and **5b**, respectively), and can be described as an exchange of thioketene units.

Scheme 6 summarizes our proposal for the solution equilibria in which the heterodinuclear Cu/Ag derivatives are involved: (a) phosphine dissociation equilibrium between complexes **6** and **7**, (b) intermolecular exchange of $[Cu(PCy_3)]^+$ and $[Ag(PCy_3)]^+$ units between molecules of **7** to give homodinuclear complexes of Cu (**2**) and Ag (**8**), and (c) exchange of thioketene units between molecules of **7** to give ligand **IV** complexes **9** and other species. Depending on the phosphine ligand these equilibria lead to the observation of different species in solution. Thus, solutions of the PCy_3 complex **6c** in $CDCl_3$ contain **7c**, free PCy_3, and small amounts of the dicopper and disilver derivatives **2c** and **8c**, respectively, which are also observed in solutions of **7c**. Probably, the great steric requirement of PCy_3 prevents the thioketene exchange between molecules of **7c** to give **9c**. Complex **6a** or **b** is in equilibrium with the dicopper complex, **2a** or **3b** (not shown in Scheme 6), the disilver complexes **8a** or **b**, the heterodinuclear complexes **9a** or **b**, containing the ligand **IV**, and unidentified species. The presence of complexes **7a** or **b** due to phosphine dissociation is also expected in these solutions, and it is reasonable to assume that they are involved in the formation of complexes **9a** and **b** because all attempts to prepare the **7a** or **b** (see above) invariably led to the formation of **9a** or **b**. This is also supported by the fact that the thioketene-exchange equilibrium observed for the homodinuclear Cu(I) complexes takes place from a bis(phosphine) derivative (**2b**) and not from the parent tris(phosphine) complex (**3b**). Moreover, the the solutions of complexes **6a** or **b** produce only limited amounts of **9a** or **b**, suggesting that the thioketene-exchange process requires the previous dissociation of phosphine to give **7a** or **b**. In view of the thioketene-exchange equilibrium represented in Scheme 5, the synthesis of complexes **9a,b** requires the simultaneous formation of the same number of equivalents of dithiolato complexes of Cu(I) and Ag(I), which would account for the unassigned NMR signals observed in the spectra of **6a,b** but whose nature could not be established. Correspondingly, the maximum possible yield of **9a**,**b** is 50% with respect to the initial equivalents of Cu and Ag.

Conclusions

The reactions of the Cu(III) complex $Pr_4N[Cu\{S_2C{=}(t\text{-Bu-fy})\}_2]$ (**1**) with $[Cu(PR_3)_4]ClO_4$ (R = Ph or To) in 1:1 molar ratio or with $AgClO_4$ and PR_3 (R = Ph, To or Cy) in 1:1:4 molar ratio lead to the formation of a new type of dithiolato complex $[MCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_3]$ (M = Cu or Ag), containing a sulfide-bridged dithiolate, formally resulting from the condensation of two $(t\text{-Bu-fy}){=}CS_2^{2-}$ ligands and removing of one S^{2-} ion. The process involves formation of $S{=}PR_3$ and probably a thioketene complex, which by a thiolato/thioketene coupling affords the new dithiolato ligand. These complexes undergo phosphine dissociation equilibria leading to the formation of the corresponding bis(phosphine) derivatives $[MCu\{[SC{=}(t\text{-Bu-fy})]_2S\}(PR_3)_2]$, which when M = Ag may undergo subsequent exchange processes to give small amounts of dicopper and disilver complexes. Some of these dinuclear complexes undergo a thioketene-exchange process leading to the formation of a dithiolato complexes and new dinuclear complexes of the type $[MCu\{[SC{=}(t\text{-Bu-fy})]_3S\}(PR_3)_2]$, containing another new type of dithiolato ligand formally resulting from the condensation of three $(t\text{-Bu-fy}){=}CS_2^{2-}$ ligands and removing of two S^{2-} ions. The present work is the first study on the reactivity of a Cu(III) 1,1-ethylenedithiolato complex. The observed reactions are unprecedented in the chemistry of dithiolato complexes and have allowed the isolation of a series of derivatives with new types of dithiolato ligands.

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 **3b**, **6b**, **6c**·$2CH_2Cl_2$, **7c**·$0.2CH_2Cl_2$·$0.8MeCN$, and **9a**·$CHCl_3$, low-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of **3b**, and ^1H NMR spectra of **6a** and **b** at different times after dissolution. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8014139

---

[22] (a) Raasch, M. S. *J. Org. Chem.* **1970**, *35*, 3470–3483. (b) Green, M.; Osborn, R. B. L.; Stone, F. G. A. *J. Chem. Soc., A* **1970**, 944–946. (c) Raasch, M. S. *J. Org. Chem.* **1972**, *37*, 1347–1356. (d) Harris, S. J.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1008–1009. (e) Umland, H.; Behrens, U. *J. Organomet. Chem.* **1983**, *273*, C39–C42. (f) Benecke, J.; Behrens, U. *J. Organomet. Chem.* **1989**, *363*, C15–C18. (g) Ziegler, W.; Wormsbächer, D.; Behrens, U. *J. Organomet. Chem.* **1992**, *431*, C11–C16.