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Copper Complexes with (2,7-Di-*tert*-butylfluoren-9-ylidene)methanedithiolate: Oxidatively Promoted Dithioate Condensation[‡]

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The reaction of $[Cu(NCMe)_4]PF_6$ with piperidinium 2,7-di-*tert*-butyl-9*H*-fluorene-9-carbodithioate (pipH)$[S_2C(t\text{Bu-Hfy})]$ (**1**; *t*Bu-Hfy = 2,7-di-*tert*-butylfluoren-9-yl), affords $[Cu_n\{S_2C(t\text{Bu-Hfy})\}_n]$ (**2**), which reacts with various P ligands to give $[Cu\{S_2C(t\text{Bu-Hfy})\}L_2]$ [L = PPh_3 (**3a**), PCy_3 (**3b**), $PiPr_3$ (**3d**); L_2 = 1,1′-bis(diphenylphosphanyl)ferrocene (dppf, **3c**), bis(diphenylphosphanyl)methane (dppm, **3e**)]. Compounds **3a**–**c** react with atmospheric oxygen and moisture in the presence of NEt_3 to give the dinuclear complexes $[Cu_2\{[SC{=}(t\text{Bu-fy})]_2S\}L_2]$ [*t*Bu-fy = 2,7-di-*tert*-butylfluoren-9-ylidene; L = PPh_3 (**4a**), PCy_3 (**4b**); L_2 = dppf (**4c**)], which contain a new dithiolato ligand formally resulting from the condensation of two dithioato ligands with loss of a sulfide ion and two protons. Neutral Cu^I dithiolate complexes of the type $[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2L_4]$ [$S_2C{=}(t\text{Bu-fy})$ = [2,7-di-*tert*-butylfluoren-9-ylidene)methanedithiolate; L = PPh_3 (**5a**), $P(C_6H_4OMe\text{-}p)_3$ (**5b**), $PiPr_3$ (**5d**) or L_2 = dppf (**5c**)] were obtained by treating **1** with $[Cu(NCMe)_4]PF_6$, the corresponding phosphane, and piperidine in a 1:2:2:1 molar ratio. The reaction of **1** with $Cu(ClO_4)_2{\cdot}6H_2O$ and $(Pr_4N)OH$ in a 2:1:2 molar ratio gives the Cu^{II} complex $(Pr_4N)_2[Cu\{S_2C{=}(t\text{Bu-fy})\}_2]$ [$(Pr_4N)_2$**6**], which readily oxidizes to the Cu^{III} complex $Pr_4N[Cu\{S_2C{=}(t\text{Bu-fy})\}_2]$ (Pr_4N**7**) in the presence of atmospheric oxygen and moisture. The salt PPN**7** [PPN^+ = $(Ph_3P)_2N^+$] was obtained from **1**, $CuCl_2{\cdot}2H_2O$, PPNCl, and piperidine in a 2:1:1:2 molar ratio under aerobic conditions. The crystal structures of **3a**, **3c**$\cdot CH_2Cl_2$, **4a**$\cdot 4Me_2CO$, and **4c**$\cdot CH_2Cl_2$ have been determined by X-ray diffraction studies.

Introduction

The importance of copper complexes and clusters with thiolato ligands is associated with their use as models for the understanding of the structure, bonding, and function of the active sites of copper–sulfur enzymes and proteins,[1–6] which perform crucial functions such as electron-transfer and dioxygen transport to redox systems and copper transport and delivery.[7–11] Among the variety of sulfur ligands employed for the synthesis of copper complexes, 1,1-ethylenedithiolates ($XYC{=}CS_2^{2-}$) and related dithio ligands have received special attention because of their ability to form high-nuclearity clusters, some of which have found industrial applications as antioxidant additives for lubricant oils.[12–20] Previously described 1,1-ethylenedithiolates that have been used for the preparation of copper complexes are limited to those with X = Y = CN (*i*-mnt), CO_2R [R = Me (dmd), Et (ded), *t*Bu (*t*Bu-ded)] and X = CN and Y = $P(O)(OEt)_2$ (cpdt). The anionic Cu^I clusters $[Cu_8(i\text{-mnt})_6]^{4-}$,[12,13,19] $[Cu_8(\text{ded})_6]^{4-}$,[14] and $[Cu_8(t\text{Bu-ded})_6]^{4-}$[15,16] stand out as the best-studied 1,1-ethylenedithiolato complexes of copper, and theoretical calculations have been carried out in order to understand the bonding in the Cu_8S_{12} core.[21,22] The tetranuclear cluster $[Cu_4(i\text{-mnt})_4]^{4-}$ has been obtained from the reaction of the sulfur-rich dithiolato cluster $[Cu_6\{S_3C{=}C(CN)_2\}_6]^{6-}$ with triphenylphosphane.[19] Clusters of higher nuclearities have been obtained by protonation of $[Cu_8(\text{ded})_6]^{4-}$ and $[Cu_8(t\text{Bu-ded})_6]^{4-}$.[15,16] A series of clusters of Cu^I with the cpdt ligand and bis(diphenylphosphanyl)methane (dppm) has also been prepared from the reaction between $[Cu_2(\text{dppm})_2(NCMe)_2](PF_6)_2$ and K_2cpdt.[23] The Cu^{II} complexes are represented by the mononuclear species $[Cu(i\text{-mnt})_2]^{2-}$,[12,24] $[Cu(\text{ded})_2]^{2-}$,[25,26] and $[Cu(i\text{-mnt})(N–N)]$ (N–N = 1,2-ethanediamines).[27] The Cu^{III} complex $[Cu(\text{ded})_2]^-$ has also been prepared by the oxidation of $[Cu(\text{ded})_2]^{2-}$ with H_2O_2, I_2, or Cu^{2+} ions.[25,26]

Part of our recent research in this field has been devoted to the coordination chemistry of the (fluoren-9-ylidene)me-

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[‡] (Fluoren-9-ylidene)methanedithiolato Complexes, 3. Part 1: Ref.[28] Part 2: Ref.[29]

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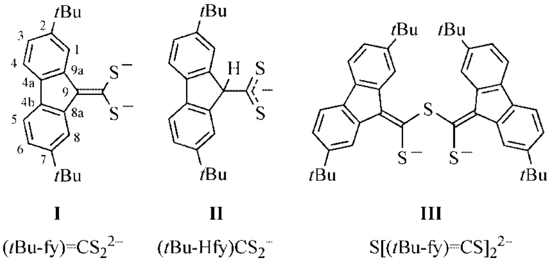
thanedithiolato ligand and its 2,7-disubstituted derivatives. These ligands have revealed remarkable differences with respect to the previously used 1,1-ethylenedithiolates; these differences are largely attributable to the absence of strongly electron-withdrawing substituents and affect the photophysical properties and redox behavior of their metal complexes.[28,29] Given the multiple coordination possibilities and stoichiometries observed for copper/dithiolate systems, we thought it of interest to carry out an initial exploration of the chemistry of copper complexes with (2,7-di-*tert*-butylfluoren-9-ylidene)methanedithiolate [(*t*Bu-fy)=CS_2^{2-} (**I**) Scheme 1], and to study the effects of the strongly electron-donating character of this ligand on their structures and reactivity. In this paper, we describe the preparation of a series of Cu^I complexes with 2,7-di-*tert*-butyl-9*H*-fluorene-9-carbodithioate [(*t*Bu-Hfy)CS_2^- (**II**), the protonated precursor of **I**] obtained from the piperidinium salt (pipH)[(*t*Bu-Hfy)CS_2] (**1**), which, upon deprotonation in the presence of an oxidizing agent, afford dinuclear complexes with the new ligand S[(*t*Bu-fy)=CS]$_2^{2-}$ (**III**), formally resulting from the condensation of two dithiolates with loss of a sulfide ion and two protons. The direct syntheses of Cu^I, Cu^{II}, and Cu^{III} complexes containing the (*t*Bu-fy)=CS_2^{2-} ligand from **1** and suitable copper precursors are reported.



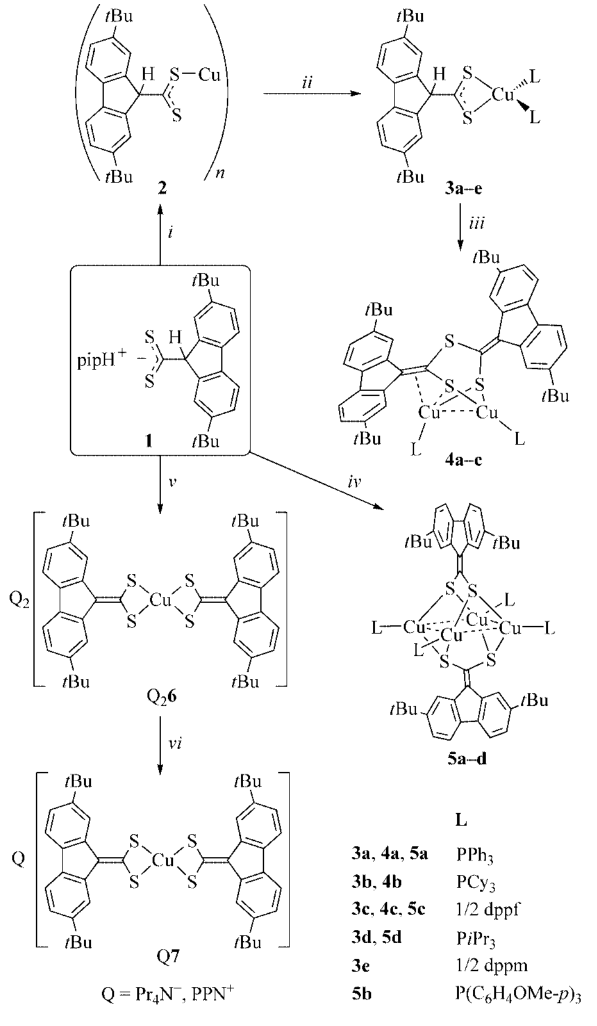
Scheme 1.

Results and Discussion

Copper(I) Complexes with the (*t*Bu-Hfy)CS_2^- Ligand

The previously described metal complexes with the (fluoren-9-yliden)methanedithiolato ligand and its 2,7-disubstituted analogs were obtained by treating appropriate metal precursors with the corresponding piperidinium fluorene-9-carbodithioate in the presence of a base. The deprotonation of the dithiolato ligand to form the corresponding dithiolate takes place after its coordination to the metal center, which increases the acidity of the H9 atom on the fluoren-9-yl moiety. In some cases, dithioato complexes have been obtained when the reactions are carried out in the absence of a base.[28] The synthesis of Cu^I complexes with (*t*Bu-Hfy)CS_2^- was undertaken in order to use them as precursors for the preparation of complexes with the dithiolato ligand (*t*Bu-fy)CS_2^{2-}.

The reaction of the piperidinium dithioate **1** with $[Cu(NCMe)_4]PF_6$ in a 1:1 molar ratio in MeCN gave the dark brown complex $[Cu_n\{S_2C(tBu\text{-}Hfy)\}_n]$ (**2**; Scheme 2), which precipitated in almost quantitative yield. Complex **2** is scarcely soluble in most organic solvents and all attempts to grow crystals suitable for X ray diffraction studies were unsuccessful. Its ^1H NMR spectrum displays only one set of signals for the dithioato ligand, suggesting a highly symmetrical oligomeric structure. A tetrameric structure has been found for the related copper(I) dithioate $[Cu_4(S_2CC_6H_4Me\text{-}p)_4]$[30] (Figure 1, a). Compound **2** was



	L
3a, 4a, 5a	PPh_3
3b, 4b	PCy_3
3c, 4c, 5c	1/2 dppf
3d, 5d	$PiPr_3$
3e	1/2 dppm
5b	$P(C_6H_4OMe\text{-}p)_3$

Scheme 2. (i) $[Cu(NCMe)_4]PF_6$; (ii) 2L; (iii) NEt_3, O_2 (air) or 1/2 1,4-benzoquinone; (iv) 2 $[Cu(NCMe)_4]PF_6$, 2L, pip; (v) 1/2 $Cu(ClO_4)_2{\cdot}6H_2O$, $(Pr_4N)OH$ or 1/2 $CuCl_2$, PPNCl, pip; (vi) O_2 (air).

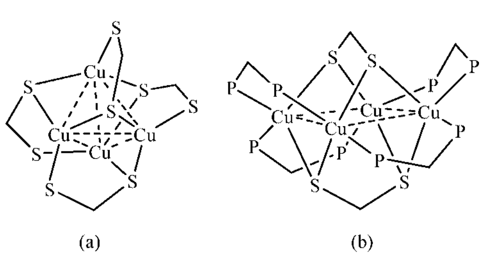


Figure 1. Structures of the Cu_4S_8 core in $[Cu_4(S_2CC_6H_4Me\text{-}p)_4]$ (a) and the $Cu_4S_4P_8$ core in $[Cu_4(cpdt)_2(dppm)_4]$ (b).

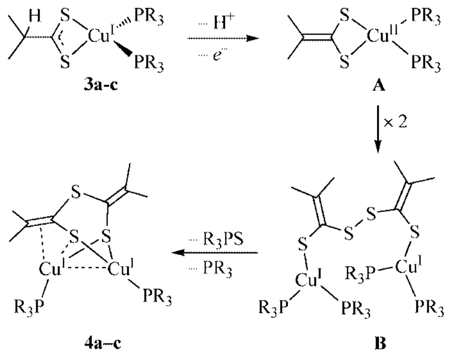
employed as starting material for the preparation of the series of complexes [Cu{S_2C(*t*Bu-Hfy)}L_2] with L = PPh_3 (**3a**), PCy_3 (**3b**), P*i*Pr_3 (**3d**), or L_2 = dppf (**3c**), dppm (**3e**). The products were obtained as salmon-pink or orange solids from the reactions of **2** with the corresponding phosphane (1:2) or diphosphane (1:1) and isolated in moderate to high yields.

Deprotonation and Oxidation of Dithioato Complexes. Dithiolate Condensation

The deprotonation of the dithioato ligand (*t*Bu-Hfy)CS_2^- in complexes **2** and **3a**–**e** was attempted by using NEt_3 as the base. The expected results of these reactions included the formation of anionic clusters. In the case of **3a**–**e**, anionic complexes of the type [Cu{S_2C=(*t*Bu-fy)}$(PR_3)_2$]$^-$ were expected as the primary products, since an analogous mononuclear complex with the *i*-mnt ligand has been described.[31] However, complexes **2** and **3a**–**e** were recovered unchanged after treatment with NEt_3 in MeCN or THF under an inert atmosphere. A different, unexpected result was obtained when the reactions were carried out in the presence of atmospheric oxygen and moisture. Thus, under these conditions, treatment of **3a** with NEt_3 in a 1:1 molar ratio in MeCN led to the gradual formation of a green solution from which a yellowish orange solid precipitated after 4 h. The X-ray structure analysis of a single crystal of this product revealed the formation of the dinuclear complex [Cu_2{[SC=(*t*Bu-fy)]$_2$S}$(PPh_3)_2$] (**4a**), which contains only one PPh_3 per Cu and a new dithiolato ligand that formally results from the condensation of two (*t*Bu-Hfy)CS_2^- ligands with loss of a sulfide ion and two protons (Scheme 2). The yield of **4a** was 67% after recrystallization. The oily residue obtained by evaporation of the supernatant contained Ph_3P=S, Ph_3P=O, and free PPh_3 as the major components, as determined by ^1H and ^{31}P NMR spectroscopy. Additionally, a very small amount of the dithiolato complex [Cu_4{S_2C=(*t*Bu-fy)}$_2(PPh_3)_4$] (**5a**; see below) was produced. The formation of **4a** also took place when stirring **3a** in MeCN under aerobic conditions in the absence of NEt_3, but the reaction was much slower. It is therefore clear that an oxidant is required for this reaction to take place and that the deprotonation does not require an added base. Finally, the reaction of **3a** with the oxidant base 1,4-benzoquinone in a 2:1 molar ratio was carried out under a nitrogen atmosphere in MeCN at room temperature. Under these conditions, the gradual formation of a yellowish orange precipitate of **4a** was observed within seven hours. The product was isolated in 73% yield after recrystallization and the compounds Ph_3P=S, 1,4-hydroquinone, and free PPh_3 were identified by ^1H and ^{31}P NMR spectroscopy as the major components present in the supernatant.

The analogous complexes [Cu_2{[SC=(*t*Bu-fy)]$_2$S}L_2] with L = PCy_3 (**4b**) or L_2 = dppf (**4c**) were similarly obtained by stirring suspensions of **3b** or **3c**, respectively, in MeCN in the presence of NEt_3 and atmospheric oxygen. The yield of **4b** (75%) was appreciably higher than of **4c** (51%) because of the formation of considerable amounts of the dithiolato complex [Cu_4{S_2C=(*t*Bu-fy)}$_2$(dppf)$_2$] (**5c**; see below). Under the same conditions, compound **2** or the dppm derivative **3e** did not give products of definite composition, while in the case of the P*i*Pr_3 derivative **3d** a mixture that contained the corresponding dithiolato complex **5d** as the main component was obtained.

A possible reaction path leading to the formation of **4a**–**c** is outlined in Scheme 3. It is very likely that in the initial steps the deprotonation and oxidation of the dithioato complexes **3a**–**c** to give a Cu^{II} intermediate (**A**) take place, which would account for the green color of the initial reaction mixtures. This species can be considered an oxidized analog of the reported Cu^I complex [Cu(*i*-mnt)$(PR_3)_2$]$^-$.[31] It is well known that the combination of Cu^{II} with thiolates usually results in reduction to Cu^I and formation of disulfides.[10,32,33] Such a process would cause intermediate **A** to dimerize and form a disulfide-bridged dinuclear species such as **B**, which would subsequently undergo sulfur abstraction by one of the phosphanes to give the final monosulfide-bridged dithiolate. 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 $R_2NC(S)SC(S)NR_2$.[34] The formation of the condensed ligand in **4a**–**c** is also related to the well-established reactions of organic disulfides with phosphanes, which afford thioethers and phosphane sulfide, although they usually require more vigorous reaction conditions, such as refluxing in high boiling point solvents.[35–37]



Scheme 3. Proposed reaction path for the formation of **4a**–**c** from **3a**–**c**. *t*Bu-fy groups have been omitted for clarity.

In contrast, similar sulfide-bridged dithiolato ligands have not been produced from previously described dithioato complexes of the type [Cu(S_2CR)$(PR'_3)_2$] containing a hydrogen atom in the β position, such as those with R = Me,[38] or CH=C(OH)C_6H_4Me-*p*.[39] Both the presence of the relatively acidic H9 hydrogen atom in (*t*Bu-Hfy)CS_2^- and the electron-donating ability of (*t*Bu-fy)=CS_2^{2-} appear to be crucial for the initial deprotonation/oxidation steps leading to **4a**–**c**.

Copper(I) Complexes with the (*t*Bu-fy)=CS_2^{2-} Ligand and Phosphanes

The neutral Cu^I complexes $[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2L_4]$ [L = PPh_3 (**5a**), $P(C_6H_4OMe\text{-}p)_3$ (**5b**) and $PiPr_3$ (**5d**) or L_2 = dppf (**5c**)] were obtained by treating **1** with $[Cu(NCMe)_4]PF_6$, the corresponding phosphane, and piperidine in a 1:2:2:1 molar ratio in MeCN (Scheme 2). The products precipitate in this solvent as bright yellow (**5a**,**b**,**d**) or yellowish orange (**5c**) microcrystalline solids and can be isolated in moderate to high yields. Compounds **5a**–**d** display a moderate stability in solution, which depends on the phosphane; thus, the $PiPr_3$ complex **5d** is the least stable and decomposes in $CDCl_3$ within 2 h, while the $CDCl_3$ solutions of the $P(C_6H_4OMe\text{-}p)_3$ complex **5b** are stable for more than 24 h. The preparation of analogous complexes with PCy_3 or dppm did not succeed under similar conditions, probably because of their lower stabilities.

The structures of **5a**–**d** could not be determined by X-ray diffraction studies because the crystals were not of sufficient quality or presented severe twinning problems. However, their composition and the copper/dithiolate/phosphane ratio were unambiguously determined by means of elemental analyses and ^1H NMR spectroscopy (see Experimental Section for details). The ^1H, ^{13}C, and ^{31}P NMR spectroscopic data are consistent with highly symmetrical structures containing equivalent dithiolato ligands and phosphanes. Given the preference of Cu^I for a trigonal planar or tetrahedral coordination geometry and its tendency to form high nuclearity thiolato complexes with extensive cuprophilic interactions, a dinuclear formulation for **5a**–**d** is unlikely. Evidence for a tetranuclear formulation was obtained from their positive-ion FAB mass spectra. The tetranuclear $[M^+]$ ions are observed with very low relative abundances for **5b** (*m*/*z* = 2368) and **5c** (*m*/*z* = 2068). Heavier ions are not observed, except for the $[M + Cu]^+$ ions. All four complexes undergo very extensive fragmentations in FAB, which result in the loss of phosphane ligands and CuL^+ units and/or the cleavage of C–S bonds to form sulfide complexes, most of which are tetranuclear. Significantly abundant fragments that support the tetranuclear formulation are $[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2L_3]^+$ for **5b**, $[Cu_4S\{S_2C{=}(t\text{Bu-fy})\}L]^+$ and $[Cu_4S\{S_2C{=}(t\text{Bu-fy})\}_2L]^+$ for **5a**,**b**, $[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2L]^+$ and $[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2]^+$ for **5a**,**d**, and $[Cu_4S\{S_2C{=}(t\text{Bu-fy})\}(\text{dppf})_2]^+$ for **5c** (see Supporting Information). Tetranuclear structures have been found for the related complexes $[M_4(\text{cpdt})_2(\text{dppm})_4]$ (M = Cu[23] and Ag[40]), $[Ag_4(i\text{-mnt})_2(\text{dppm})_4]$,[41] and $[Cu_4(CS_3)_2(\text{dppm})_4]$,[42] which have their metal atoms in a nearly planar arrangement and the dithiolato ligands acting as bridging tetradentate ligands above and below the M_4 core (Figure 1, b). The structures of **5a**–**d** probably have similar Cu_4S_4 cores but with four phosphane groups instead of eight (Scheme 2), which would be consistent with their NMR spectroscopic data.

Complexes **5a**–**d** are luminescent at room temperature in the solid state and also in solution at 77 K. Their excitation and emission properties are currently under investigation and a complete study will be reported elsewhere.

Copper(II) and Copper(III) Complexes with the (*t*Bu-fy)=CS_2^{2-} Ligand

The poorly soluble Cu^{II} complex $(Pr_4N)_2[Cu\{S_2C{=}(t\text{Bu-fy})\}_2]$ [$(Pr_4N)_2$**6**] precipitated as a brown solid upon treatment of the dithioate **1** with $Cu(ClO_4)_2{\cdot}6H_2O$ and $(Pr_4N)OH$ in a 2:1:2 molar ratio in MeCN under an inert atmosphere, (Scheme 2). Although [$(Pr_4N)_2$**6**] is air stable in the solid state, it is slowly oxidized by atmospheric oxygen to the Cu^{III} complex $[Cu\{S_2C{=}(t\text{Bu-fy})\}_2]^-$ (**7**) when suspended in MeCN or CH_2Cl_2. Thus, the green salt Pr_4N**7** was obtained almost quantitatively by bubbling air through an MeCN suspension of $(Pr_4N)_2$**6**. Alternatively, Pr_4N**7** was obtained in high yield when the reaction of **1** with $Cu(ClO_4)_2{\cdot}6H_2O$ and $(Pr_4N)OH$ was carried out under atmospheric conditions. The salt PPN**7** was similarly obtained from **1**, $CuCl_2{\cdot}2H_2O$, PPNCl, and piperidine in a 2:1:1:2 molar ratio. The only previously reported Cu^{III} complex with a 1,1-ethylenedithiolato ligand is $[Cu(\text{ded})_2]^-$, which was prepared from the oxidation of $[Cu(\text{ded})_2]^{2-}$ with H_2O_2, I_2, or Cu^{2+} ions.[25,26] In comparison, the formation of the Cu^{III} complex **7** takes place under milder conditions and represents an uncommon example of aerobic oxidation of a Cu^{II} complex. We have previously observed that the (fluoren-9-ylidene)methanedithiolato ligand and its 2,7-disubstituted derivatives facilitate the oxidation of Au^I to Au^{III} [28] and Pt^{II} to Pt^{IV},[29] which can be attributed to their stronger electron-donating character as compared with other, more commonly studied 1,1-ethylenedithiolato ligands.

Crystal Structures of the Complexes

The crystal structures of **3a** (Figure 2), **3c**·CH_2Cl_2 (Figure 3), **4a**·$4Me_2CO$ (Figure 4), and **4c**·CH_2Cl_2 (Figure 5) were solved by X-ray diffraction studies. Selected bond lengths and angles are listed in Tables 1, 2, and 3. The molecular structures of **3a** and **3c** show the copper atom in a distorted tetrahedral environment. The main distortion originates from the constraints imposed by the four-membered chelate ring, which lead to S–Cu–S angles of 74.48(2)° (**3a**) and 74.38(3)° (**3c**). The steric hindrance of the PPh_3 ligands leads to a relatively wide P(1)–Cu–P(2) angle of 129.25(3)° in **3a**. The chelating dppf ligand in **3c** adopts a staggered conformation leading to a bite angle of 112.76(4)°, which is closer to the ideal value for a tetrahedral geometry. Similar coordination environments around the Cu atom and Cu–S bond lengths have been found in the analogous dithioato complexes $[Cu(S_2CR)(PPh_3)_2]$ [R = Me,[38] Ph,[43] *p*-To,[30] C_5Me_5[44] CO_2Me[45] and $CH{=}C(OH)C_6H_4Me\text{-}p$].[39]

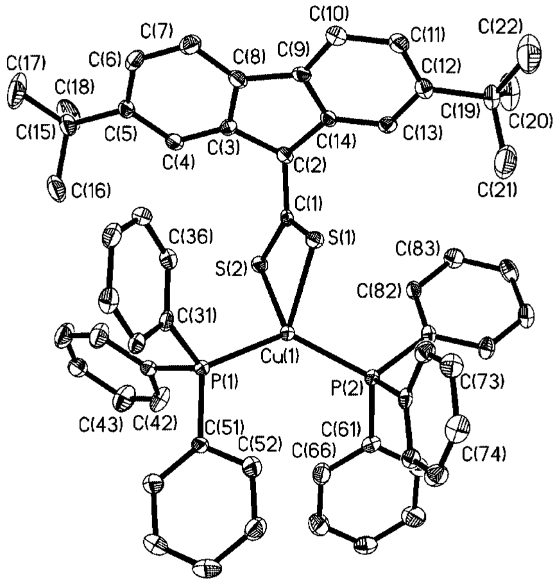


Figure 2. Thermal ellipsoid plot (50% probability) of complex **3a**. H atoms have been omitted for clarity.

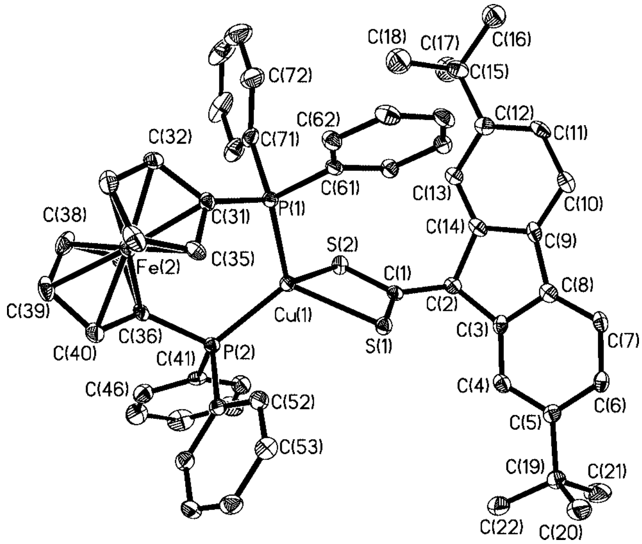


Figure 3. Thermal ellipsoid plot (50% probability) of complex **3c**. H atoms have been omitted for clarity.

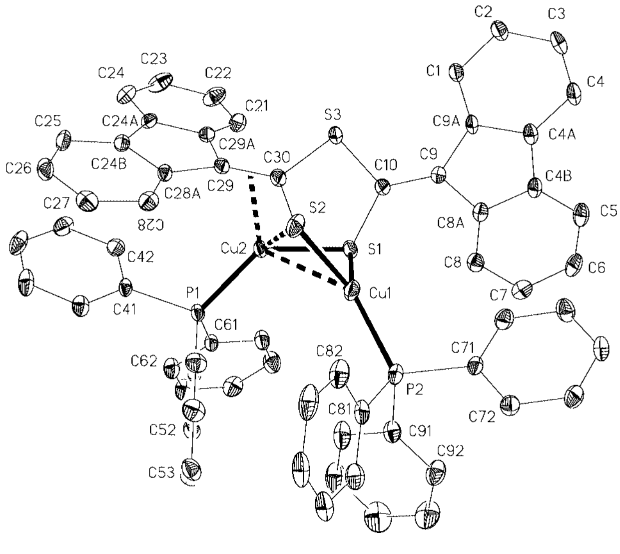


Figure 4. Thermal ellipsoid plot (30% probability) of complex **4a**. H atoms and *t*Bu groups have been omitted for clarity.

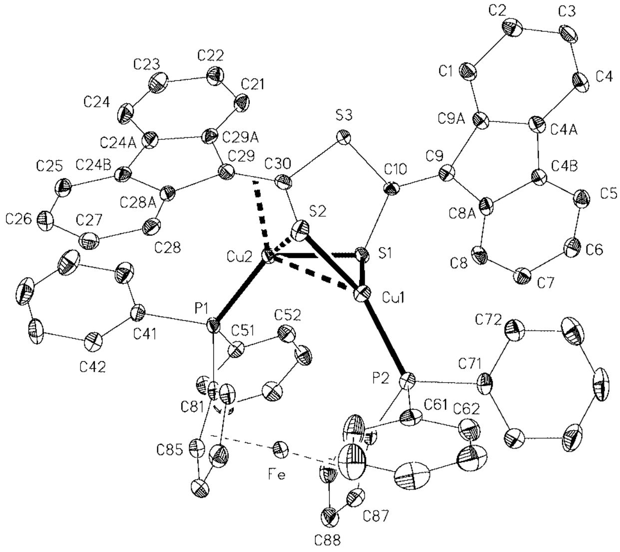


Figure 5. Thermal ellipsoid plot (50% probability) of complex **4c**. H atoms and *t*Bu groups have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **3a** and **3c**·CH_2Cl_2.

	3a	**3c**·CH_2Cl_2
Cu(1)–S(1)	2.3901(8)	2.4196(9)
Cu(1)–S(2)	2.4357(8)	2.3806(10)
Cu(1)–P(1)	2.2449(7)	2.2433(9)
Cu(1)–P(2)	2.2413(8)	2.2325(10)
S(1)–C(1)	1.674(3)	1.680(4)
S(2)–C(1)	1.693(3)	1.694(3)
C(1)–C(2)	1.520(4)	1.520(5)
S(1)–Cu(1)–S(2)	74.48(2)	74.38(3)
P(1)–Cu(1)–P(2)	129.25(3)	112.76(4)
S(1)–C(1)–S(2)	120.30(16)	118.7(2)

Complexes **4a** and **4c** exhibit essentially the same structural arrangement for the $Cu_2\{[SC{=}(t\text{Bu-fy})]_2S\}$ unit as the condensed dithiolato ligand coordinates to the two copper atoms in different ways. The atom Cu(1) is bonded to the two terminal sulfur atoms S(1) and S(2) and one PPh_3 ligand (or one of the PPh_2 units of dppf), resulting in a slightly distorted trigonal planar geometry, whereas the atom Cu(2) is attached to the other PPh_3 ligand or the second PPh_2 unit, and to the dithiolato ligand through the C(29)=C(30) double bond and the terminal S(1) atom, which thus bridges the two copper atoms. The coordination around Cu(2) is also trigonal planar if we consider the atoms S(1), P(1), and the C(29)=C(30) bond centroid. The Cu(1)–S(2) and Cu(2)–S(1) bond lengths are very similar [range 2.2156(10)–2.2659(9) Å] and slightly shorter than the Cu(1)–S(1) distance [2.3413(10) (**4a**) or 2.3298(11) Å (**4c**)]. There is also an appreciably longer Cu(2)–S(2) distance of 2.7336(9) (**4a**) or 2.7878(11) Å (**4c**), which is indicative of a much weaker interaction. The distance of Cu(1) to the

Table 2. Selected bond lengths [Å] and angles [°] for **4a**·4Me$_2$CO.

Cu(1)–P(2)	2.2053(9)	Cu(2)–S(2)	2.7336(9)
Cu(1)–S(2)	2.2576(9)	S(1)–C(10)	1.773(3)
Cu(1)–S(1)	2.3413(10)	S(2)–C(30)	1.763(3)
Cu(1)–Cu(2)	2.6999(5)	S(3)–C(10)	1.769(3)
Cu(2)–C(30)	2.087(3)	S(3)–C(30)	1.773(3)
Cu(2)–P(1)	2.2069(8)	C(9)–C(10)	1.360(4)
Cu(2)–C(29)	2.255(3)	C(29)–C(30)	1.401(4)
Cu(2)–S(1)	2.2659(9)		
P(2)–Cu(1)–S(2)	128.30(4)	C(10)–S(1)–Cu(1)	89.29(11)
P(2)–Cu(1)–S(1)	128.92(3)	Cu(2)–S(1)–Cu(1)	71.73(3)
S(2)–Cu(1)–S(1)	102.76(3)	C(30)–S(2)–Cu(1)	98.61(10)
P(1)–Cu(2)–S(1)	124.26(3)	Cu(1)–S(2)–Cu(2)	64.68(2)
P(1)–Cu(2)–S(2)	124.23(3)	C(10)–S(3)–C(30)	103.78(14)
S(1)–Cu(2)–S(2)	91.42(3)	S(3)–C(10)–S(1)	115.50(16)
C(10)–S(1)–Cu(2)	105.47(10)	S(2)–C(30)–S(3)	116.71(16)

Table 3. Selected bond lengths [Å] and angles [°] for **4c**·CH$_2$Cl$_2$.

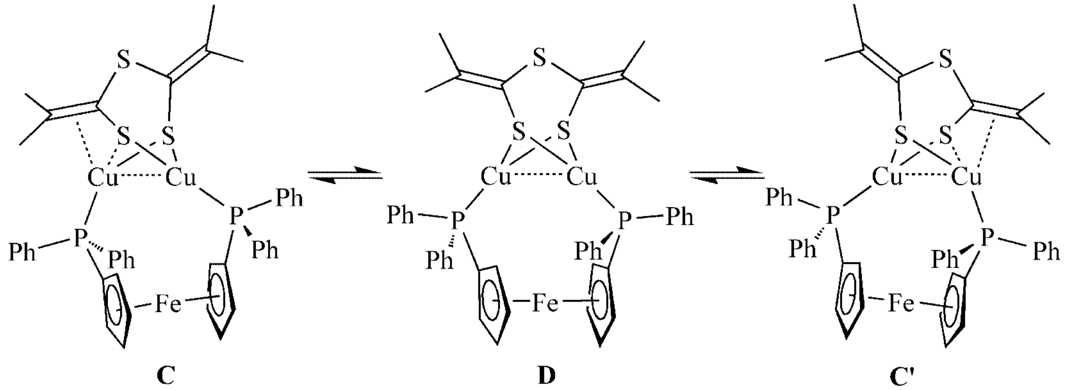
Cu(1)–P(2)	2.1821(10)	Cu(2)–S(2)	2.7878(11)
Cu(1)–S(2)	2.2156(10)	S(1)–C(10)	1.757(3)
Cu(1)–S(1)	2.3298(11)	S(2)–C(30)	1.774(4)
Cu(1)–Cu(2)	2.7568(6)	S(3)–C(10)	1.772(3)
Cu(2)–C(30)	2.114(3)	S(3)–C(30)	1.790(3)
Cu(2)–P(1)	2.2172(10)	C(9)–C(10)	1.369(5)
Cu(2)–S(1)	2.2529(9)	C(29)–C(30)	1.396(5)
Cu(2)–C(29)	2.256(3)		
P(2)–Cu(1)–S(2)	137.20(4)	C(10)–S(1)–Cu(1)	92.13(12)
P(2)–Cu(1)–S(1)	118.41(4)	Cu(2)–S(1)–Cu(1)	73.94(3)
S(2)–Cu(1)–S(1)	103.77(4)	C(30)–S(2)–Cu(1)	98.77(11)
P(1)–Cu(2)–S(1)	118.84(4)	Cu(1)–S(2)–Cu(2)	65.71(3)
P(1)–Cu(2)–S(2)	127.88(4)	C(10)–S(3)–C(30)	104.51(15)
S(1)–Cu(2)–S(2)	89.76(3)	S(1)–C(10)–S(3)	117.10(18)
C(10)–S(1)–Cu(2)	106.48(11)	S(2)–C(30)–S(3)	115.10(19)

C(29)=C(30) bond centroid of 2.056 (**4a**) or 2.072 Å (**4c**) is close to the upper limit of the range found for the majority of alkene complexes of copper(I) in the Cambridge Structural Database (1.840–2.110 Å).[46] The bond length of the uncoordinated C(9)=C(10) double bond [1.360(4) (**4a**) or 1.369(5) Å (**4c**)] is similar to the corresponding distances found for 1,1-ethylenedithiolato ligands,[28] which are usually close to the higher limit of the range found for C(sp^2)=C(sp^2) double bonds (1.294–1.392 Å),[47] whereas the C(29)–C(30) distance of 1.401(4) (**4a**) or 1.396(5) Å (**4c**) is slightly longer, as expected for a coordinated C=C bond. The Cu(1)–Cu(2) distance of 2.6999(5) (**4a**) or 2.7568(6) Å (**4c**) is slightly shorter than the sum of the van der Waals radii for Cu (2.80 Å[48]) and typical of the cuprophilic interactions found in numerous di- or polynuclear copper(I) complexes with bridging thiolato ligands.[49–53] The planes S(1)–C(10)–S(3) and S(3)–C(30)–S(2) form an angle of 75° (**4a**) or 77° (**4c**). The fluoren-9-ylidene fragments are nearly planar, with their respective mean planes being perpendicular to each other [89° (**4a**) or 90° (**4c**)] and slightly rotated with respect to the corresponding S–C–S planes. The dppf ligand in **4c** adopts an eclipsed conformation, with the P(1)–C(81) and P(2)–C(86) bonds rotated by 79° with respect to each other. This results in a large distance between both phosphorus atoms (5.275 Å) and allows the flexible dppf ligand to bridge the copper atoms in such a way that the PPh$_2$ groups occupy the same positions as the two independent PPh$_3$ ligands in **4a** (P···P = 5.438 Å).

NMR Spectra

The ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **2** and **3a**–**e** show one set of signals for the protons and carbon atoms of the dithioato ligand, which are slightly modified with respect to those of the free dithioate **1**,[54] with the 9-H resonance in the range δ = 5.35–5.68 ppm and the *C*S$_2$ resonance in the range δ = 251.5–259.3 ppm. On the basis of these data, complex **2** most probably has a highly symmetrical oligomeric structure (see above).

The crystal structures of **4a** and **4c** show that the condensed ligand contains two *t*Bu-fy groups in different environments. Because the rotation around the C9=CS$_2$ double bonds is expected to be hindered at room temperature, the two halves of each of these groups are not equivalent. Therefore, if their solid-state structures were retained in solution, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **4a**–**c** should display the resonances corresponding to four different *t*Bu groups, four sets of signals for the aromatic H and C atoms, and two signals for both the C9 and CS$_2$ atoms. Additionally, two different resonances should be expected in the ^{31}P NMR spectra. However, the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **4a**–**c** reveal that the *t*Bu-fy groups are equivalent in solution, as are the two PPh$_3$ or PCy$_3$ ligands in **4a**,**b** or the PPh$_2$ groups of the dppf ligand in **4c**. Thus, the ^{1}H NMR spectra show only two singlets for the *t*Bu groups and two sets of resonances for the aromatic protons; the two signals corresponding to the 1-H and 8-H atoms are considerably downfield-shifted, as is the case for coordinated (fluoren-9-ylidene)methanedithiolato ligands,[28] and also the most affected by the lack of symmetry of the *t*Bu-fy groups, appearing at very different chemical shifts (ranges δ = 9.61–9.71 and 8.55–8.69 ppm, respectively). The ^{13}C{^{1}H} NMR spectra show two sets of resonances for the carbon atoms of the ligand except for the C-9 and CS$_2$ atoms, each of which gives rise to only one resonance; the CS$_2$ resonance appears as a slightly broad signal for **4a**,**b**, but in the case of **4c** resolves as a triplet because of coupling with two equivalent phosphorus atoms. The ^{31}P NMR spectra show a relatively broad singlet. The dppf ligand in **4c** gives rise to six multiplets in the room temperature ^{1}H NMR spectrum corresponding to the two inequivalent Ph rings of each PPh$_2$ group, and four broad resonances corresponding to the protons of the two equivalent Cp rings. This means that the diphosphane is essentially rigid in solution and does not undergo the fluxional process observed in **5c** (see below) and other metal complexes with bridging dppf,[55–60] which involves a conformation change leading to the equivalence of the phenyl groups and the two H$_\alpha$ and H$_\beta$ atoms of the Cp rings on the NMR timescale. The absence of any dynamic process affecting the dppf ligand was further confirmed by a variable-temperature NMR study of **4c**, which revealed no changes in the ^{1}H and ^{31}P resonances arising from this diphosphane between –65 and +50 °C in CDCl$_3$.



Scheme 4. *t*Bu-fy groups have been omitted for clarity.

In view of these observations, the two possible explanations for the NMR spectroscopic data of **4a–c** are: (*i*) the existence of a dynamic process mainly affecting the $Cu_2\{[SC=(t\text{Bu-fy})]_2S\}$ unit that causes the copper atoms to interchange their coordination environments, or (*ii*) a different, symmetrical structure of the complexes in solution. The possible dynamic process is represented in Scheme 4 for **4c**. The transition from the solid state form **C** (or its equivalent **C′**) to the intermediate, C_2-symmetrical form **D** requires only minor rearrangements of the molecules involving the rupture of the relatively weak coordination of C(29)=C(30) to Cu(2) and the strengthening of the Cu(2)–S(2) interaction to form a symmetrical bridge, while retaining the conformation of the dppf ligand. However, the ^1H and ^{31}P NMR spectra of **4a–c** show that the signals arising from the condensed ligand and the phosphorus atoms do not split, even at –90 °C in CD_2Cl_2, which could be due to a very low activation energy and/or to negligible differences in the chemical shifts of the H nuclei of the inequivalent *t*Bu-fy groups (or the P nuclei of the phosphanes) in form **C**. The possibility that the actual structure in solution is form **D** would also be consistent with the experimental observations; in this case, the arrangement found in the solid-state structures would most probably be a consequence of packing forces in the crystals.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **5a–d** display very similar sets of resonances for the protons and carbon atoms of the $(t\text{Bu-fy})=CS_2^{2-}$ ligand, which indicate that all of them have similar structures with equivalent and symmetrical dithiolates. The resonances of the 1-H and 8-H atoms are typically downfield-shifted (range δ = 9.37–9.54 ppm). The resonances of the Ph and Cp protons of the dppf ligand in **5c** are observed as broad signals at room temperature, suggesting fluxional behavior. At –40 °C, the Cp resonances resolve into four signals, while the Ph rings give rise to five broad signals, indicating that the two Cp rings and PPh_2 groups of each dppf are equivalent, while the two Ph rings of each PPh_2 group are not. The fluxional behavior of a bridging dppf ligand has been observed previously and thoroughly described for other di- or polynuclear complexes.[55–60] The opposite twisting of the two halves of the ferrocene fragment around the Cp centroid–centroid axis, together with the concerted twist around the P–$C_{ipso(\mathrm{Cp})}$ and P–Cu bonds, causes the two H_α and H_β atoms and the Ph rings on each PPh_2 group to exchange their positions. The resonances of the protons of the dithiolato ligands in **5c** remain practically unchanged between –40 and 25 °C.

The ^1H NMR spectrum of the Cu^{II} complex $(Pr_4N)_2$**6** in $CDCl_3$ shows broad signals for the Pr_4N^+ cation, while the resonances corresponding to the ligand protons are not observed, which can be attributed to its paramagnetic nature. The ^1H and ^{13}C NMR spectroscopic data of the Q**7** salts (Q = Pr_4N^+, PPN^+) are fully consistent with a square-planar structure. The chemical shifts of the H and C resonances of the dithiolato ligand are very similar to those observed for the analogous Au^{III} complex.[28]

IR Spectra

The solid-state infrared spectrum of the dithioato complex **2** displays one band at 975 cm^{-1} assignable to one of the two $\nu(CS_2)$ modes,[43] while for the phosphane complexes **3a–e** the corresponding absorption appears around 1010 cm^{-1}. The dinuclear complexes **4a–c** give rise to one band associated with the $C=CS_2$ double bonds at around 1500 cm^{-1}. The expected $\nu(C=CS_2)$ band[61] arising from the $(t\text{Bu-fy})=CS_2^{2-}$ ligand in complexes **5a–d** occurs in the range 1482–1490 cm^{-1}, while for the Cu^{II} complex $(Pr_4N)_2$**6** it is observed at 1480 cm^{-1} and for the Cu^{III} salts Q**7** at 1548 (Pr_4N^+) or 1552 cm^{-1} (PPN^+). We have previously shown that the variations in the energies of the $\nu(C=CS_2)$ bands can be attributed to the oxidation state of the metal center and the nature of the ligands attached to it, which affect the strength of the π component of the $C=CS_2$ bond.[28] Usually, a higher oxidation state and/or the presence of weaker donor ligands increase the energy of the $\nu(C=CS_2)$ band, which is consistent with the high energy observed for the Cu^{III} complex. The spectra of the salts Q**7** also show one intense band at 416 (Pr_4N^+) or 420 cm^{-1} (PPN^+) assignable to the ν(Cu–S) mode.

Electronic Absorption Spectra

The UV/Visible absorption spectra of compounds **2**–**7** were measured in the range 200–700 nm in CH_2Cl_2 at 298 K. All of them display the bands arising from the aromatic part of the dithioato or dithiolato ligands at around 230, 260–270 and 300 nm.[28] The bands above 300 nm are listed in Table 4. The low intensity band centered at about 360 nm for dithioato complexes **3a**–**d** is probably the result of the modification of the band observed for the free dithioate **1b** at 346 nm, which arises from n–π* transitions within the CS_2^- group. In the case of **3e** (L_2 = dppm) this band appears at 391 nm. The spectrum of compound **2** shows two very broad bands at 393 and 438 nm, which are probably also related to these transitions.

Table 4. Electronic absorption data for compounds **2**–**7** in CH_2Cl_2 solution (ca. 5×10^{-5} M) at 298 K ($\lambda > 300$ nm).

Compound	λ [nm] (ε [$M^{-1}cm^{-1}$])
2	393, 438[a]
3a	353 (5200)
3b	360 (6000)
3c	356 (6800)
3d	357 (6100)
3e	391 (4100)
4a	369 (20900), 409 (24600), 467 (sh, 9000)
4b	372 (sh, 20700), 407 (22700), 500 (sh, 7800)
4c	367 (19800), 403 (29100), 452 (sh, 9300)
5a	415 (sh, 36300), 435 (42200)
5b	418 (sh, 36900), 440 (48000)
5c	411 (sh, 31700), 442 (37400)
5d	423 (sh, 63800), 442 (76800)
$(Pr_4N)_2$**6**	399 (36800), 430 (62500)
Pr_4N**7**	376 (16200), 397 (43600), 451 (64100)
PPN**7**	377 (29900), 397 (51300), 451 (67100)

[a] Accurate concentration and ε values could not be measured for this compound because of its very low solubility.

The absorptions of complex **4a** above 300 nm occur as broad, medium-intensity bands at 369 and 409 nm, with a shoulder at 467 nm. The analogous complexes **4b** and **4c** show a very similar pattern. The probable origins of these bands are intraligand transitions associated with the $C=CS_2$ units and ligand-to-metal charge-transfer transitions (LMCT), which are usually observed in this region for Cu^I complexes with sulfur donor ligands.[62]

The spectra of the dithiolato complexes **5a**–**d** display a very intense absorption band at around 440 nm, with a shoulder on the higher energy slope between 411 and 420 nm. Very similar absorptions have been observed for neutral Au^I–phosphane complexes containing the (fluoren-9-yliden)methanedithiolato ligand or its substituted derivatives (415 nm), which are assignable to LMCT transitions.[28]

The absorption spectra of the Cu^{III} salts Q**7** are almost identical and show two medium intensity bands at 377 and 397 nm and a very intense band at 450 nm. The two higher energy bands appear with very little differences from those in the spectra of other square-planar Au^{III} and Pt^{II} complexes containing the (*t*Bu-fy)=CS_2^{2-} ligand and can be assigned to intraligand transitions associated with the $C=CS_2$ unit. The lowest-energy band can be assigned to a metal-to-ligand charge-transfer (MLCT) transition by analogy with other isoelectronic bis(dithiolato) complexes.[24] The Au^{III} and Pt^{II} complexes with the same dithiolato ligand show this band at 410[28] or 490 nm,[29] respectively. The absorption spectrum of the Cu^{II} complex $(Pr_4N)_2$**6** is similar to those of the Q**7** salts, except for the lowest-energy band, which is observed at 430 nm.

Conclusions

The series of complexes $[Cu\{S_2C(t\text{Bu-Hfy})\}L_2]$ [L = PPh_3 (**3a**), PCy_3 (**3b**), $PiPr_3$ (**3d**); L_2 = dppf (**3c**), dppm (**3e**)] were prepared by the reaction of the oligomeric compound $[Cu_n\{S_2C(t\text{Bu-Hfy})\}_n]$ (**2**) with different P ligands. Compounds **3a**–**c** react with atmospheric oxygen in the presence of NEt_3 to give the dinuclear complexes $[Cu_2\{[SC=(t\text{Bu-fy})]_2\text{-}S\}L_2]$ [L = PPh_3 (**4a**), PCy_3 (**4b**); L_2 = dppf (**4c**)], containing a novel, sulfide-bridged dithiolato ligand, formally resulting from the condensation of two dithioato ligands with loss of a sulfide ion and two protons. The proposed reaction path for the formation of **4a**–**c** involves the initial deprotonation and oxidation of **3a**–**c**, the formation of a disulfide-bridged dinuclear species and the subsequent sulfur abstraction by one of the phosphane ligands. The first family of Cu complexes with the (2,7-di-*tert*-butylfluoren-9-ylidene)-methanedithiolato ligand has been prepared, including a series of Cu^I complexes of the type $[Cu_4\{S_2C=(t\text{Bu-fy})\}_2L_4]$ [L = PPh_3 (**5a**), $P(C_6H_4OMe\text{-}p)_3$ (**5b**), $PiPr_3$ (**5d**) or L_2 = dppf (**5c**)] and salts of the Cu^{II} complex $[Cu\{S_2C=(t\text{Bu-fy})\}_2]^{2-}$ (**6**) and the Cu^{III} complex $[Cu\{S_2C=(t\text{Bu-fy})\}_2]^-$ (**7**).

Experimental Section

General Considerations, Materials, and Instrumentation: All reactions 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 $[Cu(NCMe)_4]PF_6$ [63] and (pipH)[(*t*Bu-Hfy)CS_2][54] (**1**) 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 200, 300, or 400 spectrometers at 298 K, unless otherwise indicated. Chemical shifts are referenced to internal TMS (^1H and $^{13}C\{H\}$) or external 85% H_3PO_4 ($^{31}P\{H\}$). The assignments of the ^1H and $^{13}C\{H\}$ NMR spectra were made with the help of HMBC and HSQC experiments. Scheme 1 shows the atom numbering of the dithiolato ligand. 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 16F PC FT-IR spectrophotometer as Nujol mulls between polyethylene sheets or KBr pellets. UV/Visible absorption spectra were recorded on an Unicam UV500 spectrophotometer. FAB mass spectra were recorded on a VG Autospec 500 mass spectrometer using 3-nitrobenzyl alcohol as matrix.

$[Cu_n\{S_2C(t\text{Bu-Hfy})\}_n]$ (2): Dithioate **1** (473 mg, 0.99 mmol) was added to a solution of $[Cu(NCMe)_4]PF_6$ (359 mg, 0.96 mmol) in MeCN (20 mL). An immediate reaction was observed, with formation of a dark brown precipitate. The mixture was stirred for 30 min and the solid collected by filtration, washed with MeCN (2 × 2 mL), and vacuum-dried to give **2**. Yield: 389 mg (97 %), m.p. 184 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 975 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.61 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.47 (br., 2 H, 1-H, 8-H), 7.42 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.5 Hz, 2 H, 3-H, 6-H), 5.68 (s, 1 H, 9-H), 1.29 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 259.3 (CS_2), 150.5 (C-2, C-7), 144.6 (C-8a, C-9a), 138.5 (C-4a, C-4b), 125.4 (C-3, C-6), 121.6 (C-1, C-8), 119.2 (C-4, C-5), 71.3 (C-9), 35.0 (*C*Me$_3$), 31.5 (C*Me*$_3$) ppm. $C_{22}H_{25}CuS_2$ (417.12): calcd. C 63.35, H 6.04, S 15.37; found C 62.95, H 6.06, S 15.21.

[Cu{S$_2$C(*t*Bu-Hfy)}(PPh$_3$)$_2$] (3a): PPh_3 (90 mg, 0.34 mmol) was added to a suspension of **2** (64 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) and the mixture was stirred for 1 h. Partial evaporation of the resulting orange solution and addition of methanol (15 mL) led to the precipitation of a pale-pink solid, which was filtered off, washed with methanol (2 × 2 mL), and vacuum-dried to give **3a**. Yield: 104 mg (72 %), m.p. 120 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1011 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.84 (s, 2 H, 1-H, 8-H), 7.63 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.40 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, 3-H, 6-H), 7.28–7.22 (m, 18 H, *o*-H + *p*-H, Ph), 7.10 (m, 12 H, *m*-H, Ph), 5.38 (s, 1 H, 9-H), 1.26 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 256.4 (CS_2), 149.3 (C-2, C-7), 144.7 (C-8a, C-9a), 138.5 (C-4a, C-4b), 133.6 (C-1 + C-2, C-6, Ph), 129.3 (C-4, Ph), 128.3 (C-3, C-5, Ph), 124.4 (C-3, C-6), 123.2 (C-1, C-8), 118.8 (C-4, C-5), 71.3 (C-9), 34.9 (*C*Me$_3$), 31.6 (C*Me*$_3$) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 0.66 ppm (br). $C_{58}H_{55}CuP_2S_2$ (941.70): calcd. C 73.98, H 5.88, S 6.81; found C 73.79, H 5.94, S 6.47.

[Cu{S$_2$C(*t*Bu-Hfy)}(PCy$_3$)$_2$] (3b): This salmon-pink compound was prepared as described for **3a**, from **2** (198 mg, 0.47 mmol) and PCy_3 (270 mg, 0.96 mmol). Yield: 391 mg (84 %), m.p. 120 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1014 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.89 (br., 2 H, 1-H, 8-H), 7.57 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.35 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 3-H, 6-H), 5.35 (s, 1 H, 9-H), 1.87–1.55 (m, 30 H, Cy), 1.37 (br. s, 30 H, *t*Bu + Cy), 1.18 (br. s, 24 H, Cy) ppm. $^{13}C\{^1H\}$ NMR (300.1 MHz, $CDCl_3$): δ = 251.5 (CS_2), 148.8 (C-2, C-7), 145.2 (C-8a, C-9a), 138.5 (C-4a, C-4b), 124.1 (C-3, C-6), 123.1 (C-1, C-8), 118.5 (C-4, C-5), 71.7 (C-9), 34.9 (*C*Me$_3$), 33.5 (C-1, Cy), 31.6 (C*Me*$_3$), 30.1 (C-2, C-6, Cy), 27.8 (C-3, C-5, Cy), 26.4 (C-4, Cy) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 12.64 ppm. $C_{58}H_{91}CuP_2S_2$ (977.99): calcd. C 71.23, H 9.38, S 6.56; found C 71.12, H 9.20, S 6.26.

[Cu{S$_2$C(*t*Bu-Hfy)}(dppf)] (3c): dppf (351 mg, 0.63 mmol) was added to a suspension of **2** (262 mg, 0.63 mmol) in CH_2Cl_2 (15 mL) and the mixture was stirred for 1 h. Partial evaporation of the resulting orange solution (5 mL) and addition of pentane (30 mL) led to the precipitation of an orange solid, which was filtered off, washed with pentane (2 × 5 mL), and vacuum-dried to give **3c**. Yield: 541 mg (89 %), m.p. 198 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1010 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.87 (br. s, 2 H, 1-H, 8-H), 7.63 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.56 (m, 8 H, *o*-H, Ph), 7.39 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.3 Hz, 2 H, 3-H, 6-H), 7.32 (m, 4 H, *p*-H, Ph), 7.23 (m, 8 H, *m*-H, Ph), 5.48 (s, 1 H, 9-H), 4.27 (br., 4 H, 3-H, 4-H, Cp), 4.14 (br., 4 H, 2-H, 5-H, Cp), 1.21 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 256.5 (CS_2), 149.5 (C-2, C-7), 145.1 (C-8a, C-9a), 138.5 (C-4a, C-4b), 134.8 (vt, *N* = 31.0 Hz, C-1, Ph), 133.9 (vt, *N* = 16.8 Hz, C-2, C-6 Ph), 129.6 (C-4, Ph), 128.3 (vt, *N* = 9.6 Hz, C-3, C-5, Ph), 124.4 (C-3, C-6), 122.8 (C-1, C-8), 118.7 (C-4, C-5), 77.8 (vt, *N* = 37.7 Hz, C-1, Cp), 73.9 (vt, *N* = 10.8 Hz, C-2, C-5, Cp), 71.6 (br., C-9), 71.5 (br., C-3, C-4, Cp), 34.8 (*C*Me$_3$), 31.5 (C*Me*$_3$) ppm. $^{31}P\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = –13.33 ppm. $C_{56}H_{53}CuFeP_2S_2$ (971.51): calcd. C 69.23, H 5.50, S 6.60; found C 69.03, H 5.57, S 6.32.

[Cu{S$_2$C(*t*Bu-Hfy)}(P*i*Pr$_3$)$_2$] (3d): P*i*Pr$_3$ (167 µL, 0.88 mmol) was added to a suspension of **2** (182 mg, 0.44 mmol) in MeOH (8 mL) and the mixture was stirred for 2 h. A salmon-pink precipitate formed, which was filtered off, washed with methanol (2 × 2 mL), and vacuum-dried to give **3d**. Yield: 269 mg (84 %), m.p. 110 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1012 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.72 (s, 2 H, 1-H, 8-H), 7.58 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, 4-H, 5-H), 7.36 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, 3-H, 6-H), 5.46 (s, 1 H, 9-H), 2.13 (m, 6 H, C*H*Me$_2$), 1.35 (s, 18 H, *t*Bu), 1.22 (m, 36 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 252.8 (CS_2), 149.1 (C-2, C-7), 145.9 (C-8a, C-9a), 138.4 (C-4a, C-4b), 124.4 (C-3, C-6), 122.1 (C-1, C-8), 118.7 (C-4, C-5), 72.4 (C-9), 34.9 (*C*Me$_3$), 31.6 (C*Me*$_3$), 23.6 (*C*HMe$_2$), 20.1 (CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 21.93 ppm. $C_{40}H_{67}CuP_2S_2$ (737.60): calcd. C 65.14, H 9.16, S 8.69; found: C 65.01, H 9.23, S 8.56.

[Cu{S$_2$C(*t*Bu-Hfy)}(dppm)] (3e): This orange compound was prepared as described for **3c**, from **2** (262 mg, 0.63 mmol) and bis(diphenylphosphanyl)methane (251 mg, 0.65 mmol). Yield: 415 mg (82 %), m.p. 151 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1010 cm^{-1} (CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 7.70 (br., 2 H, 1-H, 8-H), 7.59 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.35 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 3-H, 6-H), 7.20 (br. m, 8 H, *o*-H, Ph), 7.13 (br. m, 4 H, *p*-H, Ph), 6.96 (br. m, 8 H, *m*-H, Ph), 5.61 (s, 1 H, 9-H), 3.00 (s, 2 H, CH_2), 1.23 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 256.1 (CS_2), 149.3 (C-2, C-7), 145.8 (C-8a, C-9a), 141.8 (C-4a, C-4b), 138.4 (C-1, Ph), 135.0 (C-2, C-6 Ph), 129.1 (C-4, Ph), 128.1 (C-3, C-5, Ph), 124.2 (C-3, C-6), 122.4 (C-1, C-8), 118.7 (C-4, C-5), 71.4 (C-9), 34.8 (*C*Me$_3$), 31.6 (C*Me*$_3$) (CH_2 of dppm not observed) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = –12.42 ppm. $C_{47}H_{47}CuP_2S_2$ (801.52): calcd. C 70.43, H 5.91, S 8.00; found C 70.18, H 6.21, S 7.76.

[Cu$_2${[SC=(*t*Bu-fy)]$_2$S}(PPh$_3$)$_2$] (4a). Method A: NEt_3 (22 µL, 0.17 mmol) was added to a suspension of **3a** (160 mg, 0.17 mmol) in MeCN (10 mL) and the mixture was stirred under atmospheric conditions for 4 h. The poorly soluble starting material slowly reacted to give a green solution, from which a yellowish orange solid gradually precipitated. The suspension was cooled to –15 °C and the solid collected by filtration and washed with cold MeCN (3 × 4 mL). Recrystallization from CH_2Cl_2/MeCN gave orange crystals of **4a**, which turned red upon drying under vacuum. Yield: 76 mg (67 %).

Method B: A solid mixture of **3a** (203 mg, 0.22 mmol) and 1,4-benzoquinone (12 mg, 0.11 mmol) was suspended in MeCN (10 mL) and stirred for 7 h under an atmosphere of nitrogen. The reaction took place gradually to give a yellowish orange precipitate, which was isolated and purified as described for method A to give red crystals of **4a**. Yield: 104 mg (73 %), m.p. 145 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1506 cm^{-1} (C=CS_2). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.64, 8.66 (both d, $^4J_{H,H}$ = 1.4 Hz, 2 H each, 1-H, 8-H), 7.48, 7.40 (both d, $^3J_{H,H}$ = 8.0 Hz, 2 H each, 4-H, 5-H), 7.24–7.16 (m, 10 H, 3-H, 6-H + C-4, Ph), 7.06 (m, 12 H, C-2, C-6, Ph), 6.94 (m, 12 H, C-3, C-5, Ph), 1.25, 1.14 (both s, 18 H each, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ = 148.9, 148.8 (C-2, C-7), 140.1, 139.1 (C-8a, C-9a), 138.8 (br., CS_2), 136.4, 136.2 (C-4a, C-4b), 133.5 (d, $^2J_{C,P}$ = 15.0 Hz, C-2, C-6, Ph), 132.0 (C-9), 130.9 (d, $^1J_{C,P}$ = 38.4 Hz, C-1, Ph), 129.8 (C-4, Ph), 128.4 (d, $^3J_{C,P}$ = 10.0 Hz, C-3, C-5, Ph), 123.8, 123.7, 123.0, 122.9 (C-1, C-8, C-3, C-6), 118.1, 117.9 (C-4, C-5), 34.9, 34.8 (*C*Me$_3$), 31.6, 31.4 (C*Me*$_3$) ppm.

$^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 7.38 ppm. $C_{80}H_{78}Cu_2P_2S_3$ (1324.7): calcd. C 72.53, H 5.94, S 7.26; found C 72.56, H 5.88, S 7.03.

$[Cu_2\{[SC{=}(t\text{Bu-fy})]_2S\}(PCy_3)_2]$ (4b): NEt_3 (30 µL, 0.24 mmol) was added to a suspension of **3b** (215 mg, 0.22 mmol) in MeCN (8 mL) and the mixture was stirred under atmospheric conditions for 4 h. A red precipitate gradually formed, which was filtered off and washed with MeCN (3×4 mL). The crude product was recrystallized from CH_2Cl_2/MeCN and vacuum-dried to give **4b** as a red microcrystalline solid. Yield: 113 mg (75%), m.p. 134 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1498, 1486 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.61, 8.55 (both d, $^4J_{H,H}$ = 1.5 Hz, 2 H each, 1-H, 8-H), 7.61, 7.57 (both d, $^3J_{H,H}$ = 8.0 Hz, 2 H each, 4-H, 5-H), 7.33, 7.20 (both dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 2 H each, 3-H, 6-H), 1.67 (br. m, 6 H, CH, Cy), 1.60 (br. m, 24 H, CH_2, Cy), 1.42, 1.19 (both s, 18 H each, *t*Bu), 1.16–0.99 (br. m, 36 H, CH_2, Cy) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ = 148.9, 148.7 (C-2, C-7), 140.9 (C-8a, C-9a), 140.6 (br., CS_2), 139.5 (C-8a, C-9a), 136.5, 135.8 (C-4a, C-4b), 131.7 (C-9), 123.8, 123.5, 122.9, 122.5 (C-1, C-8, C-3, C-6), 117.9, 117.8 (C-4, C-5), 35.1, 34.9 (CMe_3), 32.1 (d, $^1J_{C,P}$ = 16.8 Hz, C-1, Cy), 31.8, 31.6 (CMe_3), 30.1 (vdd, *N* = 44.1 Hz, C-2, C-6, Cy), 27.4 (d, $^3J_{C,P}$ = 11.0 Hz, C-3, C-5, Cy), 25.9 (C-4, Cy) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 21.9 ppm. $C_{80}H_{114}Cu_2P_2S_3$ (1361.0): calcd. C 70.60, H 8.44, S 7.07; found C 70.37, H 8.63, S 7.84.

$[Cu_2\{[SC{=}(t\text{Bu-fy})]_2S\}(dppf)]$ (4c): NEt_3 (21 µL, 0.17 mmol) was added to a suspension of **3c** (160 mg, 0.16 mmol) in MeCN (8 mL) and the mixture was stirred for 24 h. The reaction took place gradually to give a brown suspension. The solvent was removed under vacuum and the residue was stirred in CH_2Cl_2 (10 mL) for 7 h. The dark-brown solution was filtered through Celite and concentrated to about 4 mL. Addition of acetone (12 mL) led to the slow precipitation of an orange solid, which was filtered off, washed with acetone (3×2 mL), and vacuum-dried to give **4c**. Yield: 57 mg (51%), m.p. 200 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1504 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.71, 8.69 (both d, $^4J_{H,H}$ = 1.5 Hz, 2 H each, 1-H, 8-H), 7.77 (m, 4 H, *o*-H, Ph), 7.46–7.37 (m, 8 H, 4-H, 5-H + *m*-H, *p*-H, Ph), 7.27 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.23 (dd, $^4J_{H,H}$ = 1.7, $^3J_{H,H}$ = 8.0 Hz, 2 H, 3-H, 6-H), 7.14–7.09 (m, 4 H, 3-H, 6-H + *p*-H, Ph), 6.83 (m, 4 H, *m*-H, Ph), 6.52 (m, 4 H, *o*-H, Ph), 5.34 (br., 2 H, Cp), 4.22 (br., 2 H, Cp), 3.94 (br., 2 H, Cp), 3.47 (br., 2 H, Cp), 1.25, 1.24 (both s, 18 H each, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ = 149.0, 148.6 (C-2, C-7), 140.2 (t, $^3J_{C,P}$ = 4.1 Hz, CS_2), 140.0, 139.1 (C-8a, C-9a), 136.3 (C-4a, C-4b), 134.4 (d, $^2J_{C,P}$ = 15.5 Hz, C-2, C-6, Ph), 132.4 (d, $^1J_{C,P}$ = 38.5, C-1, Ph), 131.0 (d, $^2J_{C,P}$ = 14.5 Hz, C-2, Ph), 130.65 (C-4, Ph), 130.63 (C-9), 128.9 (C-4, Ph), 128.4 (d, $^3J_{C,P}$ = 10.4 Hz, C-3, C-5, Ph), 128.2 (d, $^3J_{C,P}$ = 9.7 Hz, C-3, C-5, Ph), 123.7, 123.6, 123.2, 123.0 (C-1, C-8, C-3, C-6), 118.3, 117.9 (C-4, C-5), 80.2 (br. d, $J_{C,P}$ = 27.8 Hz, CH, Cp), 72.9 (d, $J_{C,P}$ = 3.4 Hz, CH, Cp), 72.7 (d, $^1J_{C,P}$ = 44.1 Hz, C-1, Cp), 71.9 (d, $J_{C,P}$ = 9.9 Hz, CH, Cp), 71.4 (br., CH, Cp), 34.94, 34.89 (CMe_3), 31.62, 31.60 (CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = –1.39 ppm. $C_{78}H_{76}Cu_2FeP_2S_3$ (1354.5): calcd. C 69.16, H 5.66, S 7.10; found C 69.28, H 5.77, S 6.91.

$[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2(PPh_3)_4]$ (5a): A solid mixture of $[Cu(NCMe)_4]PF_6$ (239 mg, 0.64 mmol), PPh_3 (177 mg, 0.67 mmol), and **1** (163 mg, 0.34 mmol) was suspended in MeCN (15 mL) and treated with piperidine (36 µL, 0.36 mmol). The resulting orange suspension was stirred for 1 h, whereupon a yellow precipitate formed, which was filtered off, washed with MeCN (3×5 mL), and vacuum dried to give **5a** as a bright-yellow microcrystalline solid. Yield: 228 mg (71%), m.p. 123 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1482 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.37 (d, $^4J_{H,H}$ = 1.4 Hz, 4 H, 1-H, 8-H), 7.60 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, 4-H, 5-H), 7.25–7.18 (m, 28 H, 3-H, 6-H + *o*-H, Ph), 6.97 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, *p*-H, Ph), 6.72 (t, $^3J_{H,H}$ = 7.0 Hz, 24 H, *m*-H, Ph), 1.03 (s, 36 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 157.9 (br., CS_2), 147.7 (C-2, C-7), 140.9 (C-8a, C-9a), 135.7 (C-4a, C-4b), 133.8 (d, $^2J_{C,P}$ = 14.6 Hz, C-2, C-6, Ph), 133.3 (C-9), 132.6 (d, $^1J_{C,P}$ = 30.7 Hz, C-1, PPh_3), 129.3 (C-4 PPh_3), 128.2 (d, $^3J_{C,P}$ = 9.1 Hz, C-3, C-5, PPh_3), 124.8 (C-1, C-8), 121.3 (C-3, C-6), 116.9 (C-4, C-5), 34.8 (CMe_3), 31.8 (CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = –4.04 ppm. $C_{116}H_{108}Cu_4P_4S_4$ (2008.5): calcd. C 69.37, H 5.42, S 6.39; found C 69.16, H 5.56, S 6.25.

$[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2\{P(C_6H_4OMe\text{-}p)_3\}_4]$ (5b): This yellow compound was obtained as described for **5a**, from $[Cu(NCMe)_4]PF_6$ (235 mg, 0.63 mmol), **1** (152 mg, 0.32 mmol), and tri-*p*-methoxyphenylphosphane (227 mg, 0.64 mmol). Yield: 331 mg (89%), m.p. 167 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1498 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.53 (d, $^4J_{H,H}$ = 1.4 Hz, 4 H, 1-H, 8-H), 7.63 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, 4-H, 5-H), 7.19 (m, 28 H, 3-H, 6-H + *o*-H, C_6H_4OMe-*p*), 6.24 (d, $^3J_{H,H}$ = 7.8 Hz, 24 H, *m*-H, C_6H_4OMe-*p*), 3.45 (s, 36 H, OMe), 1.02 (s, 36 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ = 160.2 (C-4, C_6H_4OMe-*p*), 148.0 (C-2, C-7), 141.3 (C-8a, C-9a), 135.4 (C-4a, C-4b), 135.2 (d, $^2J_{C,P}$ = 16.2 Hz, C-2, C-6, C_6H_4OMe-*p*), 132.6 (C-9), 125.2 (C-1, C-8), 124.5 (d, $^1J_{C,P}$ = 35.0 Hz, C-1, C_6H_4OMe-*p*), 120.9 (C-3, C-6), 117.0 (C-4, C-5), 113.9 (d, $^3J_{C,P}$ = 10.2 Hz, C-3, C-5, C_6H_4OMe-*p*), 54.8 (OMe), 34.8 (CMe_3), 31.7 (CMe_3) ppm; CS_2 not observed. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = –8.26 ppm. $C_{128}H_{132}Cu_4P_4S_4$ (2176.8): calcd. C 64.90, H 5.62, S 5.41; found C 64.66, H 5.68, S 5.36.

$[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2(dppf)_2]$ (5c): This yellowish orange microcrystalline compound was obtained as described for **5a**, from $[Cu(NCMe)_4]PF_6$ (234 mg, 0.63 mmol), dithioate **1** (154 mg, 0.32 mmol), and dppf (177 mg, 0.32 mmol). The product was purified by recrystallization from CH_2Cl_2/acetone and dried at 60 °C for 4 h. Yield: 255 mg (78%), m.p. 198 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1490 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.54 (d, $^4J_{H,H}$ = 1.5 Hz, 4 H, 1-H, 8-H), 7.71 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, 4-H, 5-H), 7.46 (br., 16 H, *o*-H, Ph), 7.23 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.5 Hz, 4 H, 3-H, 6-H), 7.12 (br., 8 H, *p*-H, Ph), 6.91 (br., 16 H, *m*-H, Ph), 4.80 (br., 8 H, Cp), 3.86 (br., 8 H, Cp), 1.06 (s, 36 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ = 157.5 (app t, $^3J_{C,P}$ = 8.5 Hz, CS_2), 148.1 (C-2, C-7), 141.1 (C-8a, C-9a), 135.8 (C-4a, C-4b), 134.3 (br., C-1, Ph), 133.9 (C-9), 133.2 (br., C-2, C-6, Ph), 129.2 (C-4, Ph), 128.2 (d, $^3J_{C,P}$ = 9.3 Hz, C-3, C-5, Ph), 124.9 (C-1, C-8), 121.6 (C-3, C-6), 117.3 (C-4, C-5), 74.1 (d, $^2J_{C,P}$ = 36.6 Hz, C-1, Cp), 71.6 (d, $^3J_{C,P}$ = 5.2 Hz, CH, Cp), 34.9 (CMe_3), 31.9 (CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = –14.49 ppm. $C_{112}H_{104}Cu_4Fe_2P_4S_4$ (2068.1): calcd. C 65.05, H 5.07, S 6.20; found C 65.01, H 5.22, S 6.05.

$[Cu_4\{S_2C{=}(t\text{Bu-fy})\}_2(P\textit{i}Pr_3)_4]$ (5d): This bright-yellow microcrystalline compound was obtained as described for **5a**, from $[Cu(NCMe)_4]PF_6$ (335 mg, 0.90 mmol), **1** (214 mg, 0.45 mmol), and $P\textit{i}Pr_3$ (172 µL, 0.90 mmol). Yield: 241 mg (67%), m.p. 171 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1482 cm^{-1} ($C{=}CS_2$). ^1H NMR (400.9 MHz, $CDCl_3$): δ = 9.61 (s, 4 H, 1-H, 8-H), 7.60 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, 4-H, 5-H), 7.18 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, 3-H, 6-H), 1.98 (m, 12 H, $CHMe_2$), 1.35 (s, 36 H, *t*Bu), 1.14 (m, 72 H, $CHMe_2$) ppm. $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ = 22.85 ppm. $C_{80}H_{132}Cu_4P_4S_4$ (1600.27): calcd. C 60.04, H 8.31, S 8.01; found C 59.86, H 8.32, S 7.69.

Table 5. Crystallographic data for **3a**, **3c**·CH_2Cl_2, **4a**·$4Me_2CO$, and **4c**·CH_2Cl_2.

	3a	**3c**·CH_2Cl_2	**4a**·$4Me_2CO$	**4c**·CH_2Cl_2
Formula	$C_{58}H_{55}CuP_2S_2$	$C_{57}H_{55}Cl_2CuFeP_2S_2$	$C_{92}H_{102}Cu_2O_4P_2S_3$	$C_{79}H_{78}Cl_2Cu_2FeP_2S_3$
Mol. wt.	941.62	1056.36	1556.94	1439.36
T [K]	100(2)	100(2)	133(2)	133(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$Pbca$	$P\bar{1}$	$P2_1/n$
a [Å]	9.9445(5)	15.2475(4)	13.901(2)	16.998(2)
b [Å]	19.6841(9)	18.7570(5)	17.245(2)	18.785(2)
c [Å]	24.5657(12)	35.9456(11)	18.922(2)	21.544(2)
α [°]	90	90	103.664(5)	90
β [°]	90	90	96.463(5)	96.539(4)
γ [°]	90	90	100.832(5)	90
V [Å^3]	4808.7(4)	10280.3(5)	4270.0(9)	6834.8(13)
Z	4	8	2	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.301	1.365	1.211	1.399
μ [mm^{-1}]	0.646	0.980	0.657	1.087
R_1[a]	0.0414	0.0584	0.0495	0.0558
wR_2[b]	0.1046	0.1321	0.1372	0.1374

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ 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.

$(Pr_4N)_2$[Cu{S_2C=(tBu-fy)}$_2$] [$(Pr_4N)_2$6]: A previously degassed 1.0 M solution of $(Pr_4N)OH$ in water (0.60 mL, 0.60 mmol) and a solution of $Cu(ClO_4)_2·6H_2O$ (85 mg, 0.23 mmol) in MeCN (5 mL) were added successively to a solution of **1** (234 mg, 0.49 mmol) in MeCN (10 mL). Reaction was observed to give a dark-brown suspension, which was stirred for 5 min. The supernatant was decanted and the precipitate was washed with MeCN (3 × 5 mL) and vacuum-dried to give $(Pr_4N)_2$**6** as a brown powder. Yield: 208 mg (79%), m.p. 237 °C (dec.). IR (KBr): ṽ = 1480 cm^{-1} ($C=CS_2$). $C_{68}H_{104}CuN_2S_4$ (1141.4): calcd. C 71.56, H 9.18, N 2.45, S 11.24; found C 71.36, H 9.23, N 2.50, S 11.45.

Pr_4N[Cu{S_2C=(tBu-fy)}$_2$] (Pr_4N7): A solution of **1** (607 mg, 1.27 mmol) in MeCN (15 mL) was treated successively with a 1.0 M solution of $(Pr_4N)OH$ in water (1.4 mL, 1.4 mmol) and $Cu(ClO_4)_2·6H_2O$ (228.7 mg, 0.617 mmol). The resulting brown suspension was stirred for 2.5 h under atmospheric conditions, whereupon a green precipitate formed, which was filtered off, washed with MeCN (3 × 3 mL), and vacuum-dried to give Pr_4N**7**. Yield: 544 mg (92%), m.p. 233 °C (dec.). IR (Nujol): ṽ = 1548 cm^{-1} ($C=CS_2$), 416 (Cu–S). ^1H NMR [400.9 MHz, $(CD_3)_2CO$]: δ = 8.46 (d, $^4J_{H,H}$ = 1.3 Hz, 4 H, 1-H, 8-H), 7.68 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, 4-H, 5-H), 7.29 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.7 Hz, 4 H, 3-H, 6-H), 3.31 (m, 8 H, NCH_2), 1.78 (m, 8 H, CH_2), 1.39 (s, 36 H, *t*Bu), 0.95 (t, $^3J_{H,H}$ = 7.2 Hz, 12 H, Me, Pr_4N^+) ppm. $^{13}C\{^1H\}$ NMR [75.5 MHz, $(CD_3)_2CO$]: δ = 154.1 (CS_2), 149.6 (C-2, C-7), 140.2 (C-8a, C-9a), 135.7 (C-4a, C-4b), 128.2 (C-9), 122.8 (C-3, C-6), 120.7 (C-1, C-8), 119.2 (C-4, C-5), 35.4 (CMe_3), 32.1 (CMe_3) ppm. $C_{56}H_{76}CuNS_4$ (955.03): calcd. C 70.43, H 8.02, N 1.47, S 13.43; found C 70.66, H 8.29, N 1.50, S 13.79.

PPN[Cu{S_2C=(tBu-fy)}$_2$] (PPN7): Piperidine (46 µL, 0.46 mmol) and $CuCl_2·2H_2O$ (34 mg, 0.20 mmol) were added successively to a solution of **1** (212 mg, 0.45 mmol) and PPNCl (130 mg, 0.23 mmol) in MeCN (15 mL). The resulting red solution was stirred for 1 h under atmospheric conditions, after which time a green solid precipitated. The product was filtered off, washed with ethanol (3 × 2 mL) and diethyl ether (2 mL), and vacuum-dried to give PPN**7**. Yield: 184 mg (63%), m.p. 238 °C (dec.). IR (Nujol): ṽ = 1552 cm^{-1} ($C=CS_2$), 420 (Cu–S). ^1H NMR [400.9 MHz, $(CD_3)_2CO$]: δ = 8.46 (d, $^4J_{H,H}$ = 1.4 Hz, 4 H, 1-H, 8-H), 7.72–7.65 (m, 22 H, 4-H, 5-H + PPN$^+$), 7.56–7.51 (m, 12 H, PPN$^+$), 7.28 (dd, $^4J_{H,H}$ = 1.7, $^3J_{H,H}$ = 8.0 Hz, 4 H, 3-H, 6-H), 1.38 (s, 36 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR [75.5 MHz, $(CD_3)_2CO$]: δ = 154.3 (CS_2), 149.6 (C-2, C-7), 140.3 (C-8a, C-9a), 135.7 (C-4a, C-4b), 128.2 (C-9), 122.7 (C-3, C-6), 120.7 (C-1, C-8), 119.1 (C-4, C-5), 35.4 (CMe_3), 32.1 (CMe_3) ppm. $C_{80}H_{78}CuNS_4$ (1245.3): calcd. C 73.50, H 6.01, N 1.07, S 9.81; found: C 73.50, H 5.80, N 1.10, S 9.52.

X-ray Structure Determinations: Crystals of **3a**, **3c**·CH_2Cl_2, **4a**·$4Me_2CO$, and **4c**·CH_2Cl_2 suitable for X-ray diffraction studies were obtained from chloroform/pentane (**3a**), CH_2Cl_2/hexane (**3e**), acetone/hexane (**4a**), or CH_2Cl_2/pentane (**4c**). Numerical details are presented in Table 5. The structures of **3a** and **3c** were measured on a Bruker Smart APEX diffractometer, and those of **4a** and **4c** on a Bruker SMART 1000 CCD diffractometer. Data were collected using monochromated Mo-*Kα* radiation in *ω*-scan mode. The structures were solved by direct methods and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Restraints to local aromatic ring symmetry or light-atom displacement factor components were applied in some cases. The methyl groups were refined using rigid groups, and the other hydrogen atoms were refined using a riding model. *Special features of refinement*: For compound **3a**, the Flack parameter is 0.047(10). For compounds **3c**, **4a**, and **4c** the Me groups of one *t*Bu group are disordered over two positions. The solvent in the crystals of **4a** was so badly resolved that no sensible refinement model could be developed. For this reason the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands) was used to remove the effects of the solvent mathematically. The solvent content of four acetone molecules is only an approximate estimate. The dichloromethane molecule in **4c** is disordered over two positions.

CCDC-277675 (**3a**) -277674 (**3c**·CH_2Cl_2), -277676 (**4a**·$4Me_2CO$), and -277673 (**4c**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Positive ion FAB mass spectra of **5a**–**d**.

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