Bond Stretching and Redox Behavior in Coinage Metal Complexes of the Dichalcogenide Dianions [(SPh2P)2CEEC(PPh2S)2]2− (E=S, Se): Diradical Character of the Dinuclear Copper(I) Complex (E=S)

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Bond Stretching and Redox Behavior in Coinage Metal Complexes of the Dichalcogenide Dianions [(SPh₂P)₂CEEC(PPh₂S)₂]₂⁻ (E = S, Se): Diradical Character of the Dinuclear Copper(I) Complex (E = S)

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**Abstract:** The metathetical reactions of (a) \([\text{Li(TMEDA)}]_2[(S)C(PPh_2S)_2] (\text{Li}_2\text{3c})\) with \(\text{CuCl}_2\) and (b) \([\text{Li(TMEDA)}]_2[(SPh_2P)_2CSSC(PPh_2S)_2] (\text{Li}_2\text{4c})\) with two equivalents of \(\text{CuCl}\) both afford the binuclear Cu(I) complex \(\{\text{Cu}_2[(SPh_2P)_2CSSC(PPh_2S)_2]\}\) \((\text{5c})\). The elongated \((\text{C})S\text{−S}(\text{C})\) bond (ca. 2.54 and 2.72 Å) of the dianionic ligand observed in the solid-state structure of \(\text{5c}\) indicate the presence of diradical character as supported by theoretical analyses. The treatment of \([\text{Li(TMEDA)}]_2[(SPh_2P)_2CSeSeC(PPh_2S)_2] (\text{Li}_2\text{4b})\) and \(\text{Li}_2\text{4c}\) with \(\text{Ag(OSO}_2\text{CF}_3\) produce the analogous Ag(I) derivatives, \(\{\text{Ag}_2[(SPh_2P)_2CEEC(PPh_2S)_2]\}\) \((\text{6b, E = Se; 6c, E = S})\), respectively. The diselenide complex \(\text{6b}\) exhibits notably weaker Ag−Se(C) bonds than the corresponding contacts in the Cu(I) congeners, and the \(\text{31P}\) NMR data suggest a possible isomerization in solution. In contrast to the metathesis observed for Cu(I) and Ag(I) reagents, the reactions of \(\text{Li}_2\text{4b}\) and \(\text{Li}_2\text{4c}\) with \(\text{Au(CO)Cl}\) involve a redox process in which the dimeric dichalcogenide ligands are reduced to the corresponding monomeric dianions, \([\text{(E)C(PPh}_2\text{S)}_2]^{2−} (\text{3b, E = Se; 3c, E = S})\), and one of the gold centers is oxidized to generate the mixed-valent \(\text{Au(I)/Au(III)}\) complexes, \(\{\text{Au[(E)C(PPh}_2\text{S)}_2]\}_2 (\text{7b, E = Se; 7c, E = S})\), with relatively strong aurophilic Au(I)···Au(III) interactions. The new compounds \(\text{5c, 6b,c}\) and \(\text{7b,c}\) are characterized in solution by NMR spectroscopy and in the solid state by X-ray crystallography \((\text{5c, 6b, 7b and 7c})\) and by Raman spectroscopy \((\text{5c and 6c})\). The UV-Visible spectra of coinage metal complexes of the type \(\text{5, 6 and 7}\) are discussed in the light of results from theoretical analyses using time-dependent density functional theory.
Introduction

The recent development of an efficient synthetic route to the dilithium derivative of bis(thiophosphinoyl)methanediide, \([\text{C(PPh}_2\text{S)}_2]^{2-}\) (1), by Le Floch and co-workers has opened the way for wide-ranging investigations of this intriguing dithio PCP-bridged ligand. A variety of complexes with main group and transition metals, as well as with lanthanides and actinides, have revealed strong metal-carbon interactions. In addition, the mild oxidation of the dianion 1 with \(\text{C}_2\text{Cl}_6\) or \(\text{I}_2\) produced stable, monomeric or dimeric carbenoids, or a novel six-membered \(\text{C}_2\text{P}_2\text{S}_2\) ring in \([(\text{SPh}_2\text{P})_2\text{C}(\text{PPh}_2\text{S})_2]\) via a \(\text{P}\rightarrow\text{C}\) sulfur-transfer process. Similarly, our recent investigations of the isoelectronic, diseleno monoanion, \([\text{HC(PPh}_2\text{Se)}_2]^-\) (2), disclosed unusual carbon-centered reactivity. While the metathetical reactions of \([\text{Li(TMEDA)}]_2\) with \(\text{M(II)Cl}_2\) \((\text{M} = \text{Zn}, \text{Hg})\) afforded the expected homoleptic group 12 complexes with \(\text{Se},\text{Se}'\)-chelated ligands, an unprecedented selenium-proton exchange combined with a redox disproportionation occurred in reactions with group 14 and 16 element dihalides \((\text{M} = \text{Sn}, \text{Te})\) to give \(\text{M(IV)}\) complexes of the novel triseleno dianion \([(\text{Se})\text{C(PPh}_2\text{Se)}_2]^{2-}\) (3a). In a related transformation, mild thermolysis of the mononuclear Hg(II) derivative of 2, \(\text{Hg}[\text{HC(PPh}_2\text{Se)}_2]\), produced a dinuclear Hg(II) complex of 3a, while monomeric Pb(II) complexes of 3b and 3c have been attained by chalcogen insertion into the Pb–C bond of dimeric Pb(II) complexes of 1. Intriguingly, the reaction of dithio analogue of the monoanion 2, \([\text{Li(THF)(Et}_2\text{O)}]_2[\text{HC(PPh}_2\text{S)}_2]\), with group 13 halides \(\text{MCl}_3\) \((\text{M} = \text{Al}, \text{Ga}, \text{In})\) in a 2:1 molar ratio produced the dianion 1 as the \(\text{S},\text{C},\text{S}\)-bonded dimers \([\text{MCl}\{\text{C(PPh}_2=\text{S)}\}_2]\) via a process that probably involves metathesis followed by dehydrochlorination by the second equivalent of the lithium reagent.

These fascinating and structurally diverse complexes prompted us to design a direct synthesis of the novel trichalcogeno dianions, \([(\text{E})\text{C(PPh}_2\text{S)}_2]^{2-}\) (3b, \(\text{E} = \text{Se};\) 3c, \(\text{E} = \text{S})\), by using Le Floch’s dianion 1 in a reaction with elemental sulfur or selenium. The all-selenium derivative 3a cannot be obtained via this route because of the unavailability of \(\text{Li}_2[\text{C(PPh}_2\text{Se)}_2]\) owing to cleavage...
of P-Se bonds by RLi reagents.\textsuperscript{[7]} Our investigations of the one-electron oxidation of \(3b, c\) generated the novel dichalcogenides, \([(S\text{Ph}_2\text{P})_2\text{CEEC(PPh}_2\text{S}_2)_2]^{2-}\) (\(4b, E = \text{Se}\); \(4c, E = \text{S}\)), which are formally dimers of the corresponding radical anions \([(E)\text{C(PPh}_2\text{S}_2)_2]^{-}\) with moderately elongated (by ca. 8\%) central chalcogen-chalcogen bonds.\textsuperscript{[10]} In a preliminary communication, we described the generation of dinuclear Cu(I)/Cu(I) complexes of the type \(5\) by three different routes: (a) treatment of monoanion \(2\) with CuCl\(_2\) via proton-selenium exchange and a redox process (\(5a\)), (b) the redox reaction of the monomeric dianion \(3b\) with CuCl\(_2\) (\(5b\)), and (c) metathesis of dimeric dianion \(4b\) with CuCl (\(5b\)).\textsuperscript{[11]} The \(\eta^2,\eta^2\)-Se\(_2\) bonding motif established for complexes \(5a\) and \(5b\) represents a new coordination mode for generic RSe–SeR ligands.\textsuperscript{[12]} Coordination of \(4a\) and \(4b\) to the two copper centers resulted in a (further) elongation of the central selenium-selenium bond compared to the corresponding distance in the terminally \(E, E'\)-chelated Li\(^+\) derivatives.\textsuperscript{[10, 11]}

Metal complexes of the generic bis(organochalcogenides), RE–ER (E = S, Se), have attracted attention as biological models that can simulate, for example, redox processes and catalytic functions displayed by natural enzymes.\textsuperscript{[13]} In part, this is due to the propensity of these systems to undergo oxidative addition with transition metals resulting in chalcogen-chalcogen bond cleavage,\textsuperscript{[14]} therefore simulating, for example, biologically significant compounds with copper-disulfide interactions.\textsuperscript{[15]} Moreover, despite the toxicity of some organoselenium compounds, many of these systems have a significant role in biochemical processes ranging from antioxidants to anticancer and antiviral agents, and, in some cases, they also have shown therapeutic potential.\textsuperscript{[13\text{a}]} In view of the possibility of providing insights into the biologically important redox processes and with the potentially versatile coordination chemistry of the dichalcogenide ligand systems \(4b\) and \(4c\) in mind,\textsuperscript{[2a, 8, 10, 11]} we have now carried out a comprehensive investigation of their coinage metal complexes. In this contribution, we report the synthesis, spectroscopic and structural characterization of the dinuclear Cu(I)/Cu(I) complex \({\text{Cu}}_2[\eta^2,\eta^2-(\text{SPh}_2\text{P})_2\text{CSSC(PPh}_2\text{S}_2)_2]\) (\(5c\)), the dinuclear Ag(I)/Ag(I) complexes \({\text{Ag}}_2[\eta^2,\eta^2-(\text{SPh}_2\text{P})_2\text{CEEC(PPh}_2\text{S}_2)_2]\) (\(6b, E = \text{Se}\); \(6c, E = \text{S}\)) and
the mixed oxidation state Au(I)/Au(III) complexes \{Au[S,S’-(E)C(PPh\textsubscript{2}S)\textsubscript{2}]Au[E,E’,S,S’-(E)C(PPh\textsubscript{2}S)\textsubscript{2}]\} (7b, E = Se; 7c, E = S). The solid-state structures of 5c, 6b and 7b,c have been determined and their bonding is discussed in the light of results from theoretical calculations. The coinage metal complexes 5a-c, 6b,c and 7b,c were characterized in solution by NMR and Visible spectra. In the case of the Ag(I)/Ag(I) complex 6b, the variable temperature \textsuperscript{31}P NMR spectra provide evidence for fluxional behavior involving two isomers. Time dependent density functional theory data were used to interpret the transitions in the experimental electronic spectra.

Results and discussion

Synthesis and X-ray structure of {Cu\textsubscript{2}[(SPh\textsubscript{2}P)\textsubscript{2}CSSC(PPh\textsubscript{2}S)\textsubscript{2}]} (5c). In the preliminary communication we established that the dinuclear Cu(I)/Cu(I) complexes 5a and 5b displayed a significantly elongated central Se–Se contacts (ca. 15% longer than a typical Se–Se single bond of 2.34 Å).\textsuperscript{11} In view of this intriguing structural feature, we were interested in investigating the effect of changing the carbon-bound chalcogen to sulfur in order to assess the influence of Cu(I) coordination on the nature of the S–S linkage. Specifically, does metal coordination lead to bond stretching or complete cleavage of the S–S bond and subsequent formation of two radical anions, [(S)C(PPh\textsubscript{2}S)\textsubscript{2}]\textsuperscript{−}? With this in mind, the reactions between (a) the monomeric dianion 3c and Cu(II)Cl\textsubscript{2} and (b) the dimeric dianion 4c with two-equivalents of Cu(I)Cl were carried out (Scheme 1). As in the case of the selenium-containing systems,\textsuperscript{11} the reactions proceeded cleanly at -80 °C to afford a dark blue powder in good yields. The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum of the product from both reactions displayed a singlet at 59.6 ppm, cf. δ 59.5 for 5b,\textsuperscript{11} suggesting the formation of the same compound (possibly 5c) in both reactions.

Single crystals suitable for X-ray crystallography were obtained by recrystallization of the blue product from a CH\textsubscript{2}Cl\textsubscript{2} solution. The structural determination confirmed the identity of this product as {Cu\textsubscript{2}[(SPh\textsubscript{2}P)\textsubscript{2}CSSC(PPh\textsubscript{2}S)\textsubscript{2}]} (5c), which crystallized as the CH\textsubscript{2}Cl\textsubscript{2} solvate
[5c(CH₂Cl₂)₂] isostructural with the selenium-containing congeners 5a and 5b. The two four-coordinate Cu(I) centers in complex 5c are S,S’-chelated by phosphorus- and carbon-bound sulfur atoms in each half of the ligand (Figure 1). Analogously to the structure of 5b, the crystal lattice of 5c(CH₂Cl₂)₂ contains two independent molecules with mostly small discrepancies in bond parameters (Table 2). The average C−P, P−S and Cu−S(P) bond lengths of ca. 1.77, 2.01 and 2.24 Å in 5c, as well as the bond angles involving these atoms, are comparable with the corresponding distances in the diselenido analog 5b (and in the all-selenium derivative 5a, where appropriate). These parameters are also similar to those found for the Li⁺ derivative [Li(TMEDA)₂4c, thus indicating the presence of the dimeric dianion 4c in the all-sulfur Cu(I) complex 5c. Most notably, however, the (C)S−S(C) bond lengths of 2.540(4) Å (molecule A) and 2.720(3) Å (molecule B) exhibit a significant disparity of ca. 0.18 Å, and these values are in the same range as the (C)Se−Se(C) distances of 2.610(2)-2.688(2) Å in 5a and 5b, indicative of a much weaker chalcogen-chalcogen interaction in 5c. The (C)S−S(C) contacts in 5c are elongated by 0.32 and 0.50 Å, respectively, compared to the corresponding distance in the dilithium reagent 4c, and they are up to 32% longer than a typical S−S single bond (ca. 2.06 Å). For comparison, the weak (C)S−S(C) contacts in 5c are in the same range as those found for transannular S⋯S interactions in eight-membered S-N rings, e.g. 2.60 Å in the cage molecule S₄N₄ and values of 2.43-2.55 Å for the bicyclic compounds 1,5-R₄P₂N₄S₂ (R = alkyl, aryl), for which diradical character has been suggested. Side-on bonded μ-η²,η²-disulfido dinuclear Cu(II)/Cu(II) complexes of the naked S₂ ligand exhibit S–S bond distances in the range 2.07-2.17 Å, while the S–S separation in the trigonal bipyramidal trication [(tmedaCu)₃S₂]³⁺ is 2.73 Å.

Close examination of the bond parameters in the selenium derivatives 5a and 5b revealed a correlation between the shortest Cu−Se(C) contact and the (C)Se−Se(C) interaction in which the elongation of the former results in a strengthening of the latter. A similar trend is observed between the two discrete molecules in the structure of 5c(CH₂Cl₂)₂; the weaker Cu1−S5A contact of
2.361(2) Å in molecule A gives rise to the stronger S5···S5A interaction of 2.540(4) Å, cf. Cu2–S6 of 2.284(2) Å and S6···S6A of 2.720(3) Å in molecule B. However, the bond orders of the Cu–Se contacts in 5a and 5b are ca. 0.95-1.25 and the corresponding Cu–S bond orders in 5c are in a similar range at ca. 1.03-1.32.[24]

Synthesis of \{Ag_2[(SPh_2P)_2CEEC(PPh_2S)_2]\} (6b, E = Se; 6c, E = S); X-ray structure and fluxional behavior of 6b. In the light of the fascinating chalcogen-chalcogen bond elongations observed for the dinuclear Cu(I)/Cu(I) complexes 5b,c, we have investigated the synthesis of the analogous Ag(I) complexes of the dimeric dianions 4b and 4c. The reactions of the dilithium derivatives of 4b and 4c with AgOSO_2CF_3 in a 1:2 molar ratio (Scheme 1) were performed in THF at -80 °C and they resulted in rapid precipitation of a brownish-red (6b) and an orange (6c) powder, respectively. The selenium derivative 6b was identified in the solid state by a single crystal X-ray structural determination after recrystallization from CH_2Cl_2 solution. However, X-ray quality crystals of the sulfur congener 6c were not obtained, despite numerous attempts, owing to the very poor solubility of this product.

The molecular structure of \{Ag_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]\} (6b) is depicted in Figure 2, and the pertinent bond parameters are summarized in Table 2. The replacement of the Cu(I) centers in 5b with Ag^+ cations does not have a significant influence on the overall geometry of the dinuclear complex 6b. Expectedly, the bond angles involving the larger silver atom in 6b are somewhat wider than in the copper analogs 5, but the differences in bond parameters involving C, P and S atoms are insignificant. However, the Ag···Se(C) distances of 2.856(1) and 3.200(1) Å in 6b show a much larger asymmetry than the corresponding metal-chalcogen bonds in the copper complexes 5a-c. In addition, even the stronger Ag···Se(C) contact displays a bond order of only 0.51,[24] which results in a (C)Se−Se(C) bond shorter by ca. 0.15 Å than that in the copper congeners 5a,b (cf. bond orders of 0.95-1.32 for Cu(I) complexes). Both the (C)Se−Se(C) distance and the C−Se bonds in 6b are
identical to those in the dilithium derivative $[\text{Li(TMEDA)}]_24b$, in which the metal cations are $S,S'$-chelated by each terminus of the dianionic ligand $4b$.$^{[10]}$

In contrast to the copper complexes $5a-c$ and to the all-sulfur silver complex $6c$, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the selenium derivative $6b$ in CD$_2$Cl$_2$ displays two singlets at $\delta$ 57.7 and 53.1 in a ca. 1:1 ratio at room temperature. The former signal is close to the single resonance observed at $\delta$ 56.5 for the sulfur congener $6c$ and it also resembles the value of ca. $\delta$ 59.5 found for the copper complexes $5b$ and $5c$.$^{[11]}$ While the high-field singlet approaches the chemical shift of ca. $\delta$ 50.5 reported for the dilithium derivatives $[\text{Li(TMEDA)}]_24b$ and $[\text{Li(TMEDA)}]_24c$. When the solution of $6b$ is cooled, the resonance at $\delta$ 53.1 gradually disappears and at -40 °C only the slightly shifted singlet at $\delta$ 57.5 is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Warming the solution back to 23 °C results in the reappearance of the higher field resonance in a manner in which the ratio of the two singlets is approximately the same at each temperature as it was upon cooling, i.e. 50/50 at 23 °C, 60/40 at 0 °C, 65/35 at -10 °C, 75/25 at -20 °C and 85/15 at -30 °C.

The relatively long (weak) Ag···Se(C) distances in the solid-state structure of $6b$ (Table 2) hint at two plausible explanations for the two singlets seen at room temperature. In the first proposal the two weakest silver···selenium contacts (Ag1···Se1A and Ag1A···Se1 in Figure 2) are cleaved in solution to afford a tetracyclic compound $6b'$ (Scheme 2) with inequivalent phosphorus atoms as a part of five- and six-membered rings, respectively. However, the inequivalent phosphorus atoms of a –Ph$_2$PCPPh$_2$- unit in related compounds typically result in two mutually coupled doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum owing to the $^2J(^{31}\text{P},^{31}\text{P})$ coupling$^{[7, 8]}$ and this coupling is not resolved for $6b$ despite the relatively narrow signals (half-width of ca. 40 Hz at 23 °C). In addition, the steady disappearance of the singlet at $\delta$ 53.1 when temperature is lowered is inconsistent with the presence of isomer $6b''$, which would be expected to persist at lower temperatures.

An alternative explanation of the variable temperature NMR data involves the disruption of all four Ag···Se(C) contacts in $6b$ to give $6b''$ (see Scheme 2), which is in a temperature-dependent
equilibrium with $6b$ in solution. Thus, we tentatively assign the observed $^{31}$P NMR signals at room temperature to the presence of two isomers, $6b$ and $6b''$, and suggest that $6b''$ is gradually converted into $6b$ as the temperature of the solution is lowered.\[26] This explanation implies that the asymmetric $\mu$-$\eta^2;\eta^2$-Se$_2$ coordination observed for $6b$ in the solid state becomes symmetrical in solution so that only one $^{31}$P resonance at $\delta$ 57.5 is observed, cf. similar behavior in the Cu(I) complexes $5a$-$c$.

The close proximity of the singlet at $\delta$ 56.5 for the all-sulfur derivative $6c$ to the low-field resonance of the selenium analogue $6b$ and the absence of a second $^{31}$P resonance for $6c$ points toward a similar structural arrangement with that of $6b$ (Figure 2), possibly with somewhat stronger Ag···S(C) interactions which preclude isomerization in solution.

The solid-state Raman spectrum of $6c$ displays fundamental vibrations comparable to those of the copper(I) analogue $5c$, cf. Figure S7 and Table S1 in Supporting Information, therefore suggesting structural similarity between the all-sulfur complexes. A number of bicyclic and cage compounds with weak transannular S···S contacts in the range 2.40-2.71 Å and corresponding $\nu$(S–S) stretching vibrations of 186-260 cm$^{-1}$ have been reported.\[16-18] Although the S-S stretching mode typically gives rise to strong signals in Raman spectra, calculated fundamental vibrations often reveal contributions to the potential energies from bending and torsion modes, and no vibration with 100% $\nu$(S–S) stretching mode is observed, e.g. in $S_4N_4$ vibrations at 201 and 218 cm$^{-1}$ exhibit 58 and 33 % contribution, respectively, from transannular $\nu$(S–S) stretching.\[16b] Consequently, the strong vibrations between 185 and 284 cm$^{-1}$ observed in the Raman spectrum of $5c$ potentially have contributions arising from the weak (C)S···S(C) interaction (2.54-2.72 Å in the solid-state structure, Table 2). The corresponding signals for the silver analogue $6c$ span a slightly broader range of 187-317 cm$^{-1}$, possibly indicating a somewhat stronger (C)S···S(C) contact.
**Electronic structures of 5a-c and 6b,c.** To investigate the bonding observed for compounds 5 and 6, theoretical calculations were first performed for the all-sulfur parent system, \{Cu\((\text{SH}_2\text{P})_2\text{CSSC(Ph}_2\text{S)}_2\)\} (5d), in which, for simplicity, the phenyl groups were replaced with hydrogen atoms. At the PBE1PBE/def-TZVP level of theory, two minima were found on the singlet potential energy surface (PES). One of them has \(C_{2h}\) symmetry with virtually identical Cu···S(C) and (C)S···S(C) distances of 2.507 and 2.496 Å, respectively. The other optimized minimum displays a distinct asymmetry in the key bond parameters, resulting in shortening of the (C)S···S(C) bond to 2.335 Å, two markedly different Cu···S(C) interactions of 2.376 and 3.061 Å, and an overall \(C_1\) point group. This is reminiscent of the bonding features observed for the central \(E_2M_2\) unit in the X-ray crystal structures of 5a-c and 6b which display a differing range of asymmetry dependent on the identity of the group 11 and 16 elements (vide supra). Considering the total energies, the optimized isomers of 5d are virtually identical with an internal energy separation favoring the \(C_1\) symmetric form by only a few kJ mol\(^{-1}\).

The electronic structures of the two geometrical isomers of 5d expectedly reflect the distinct features in their bonding patterns. Most notably, the frontier molecular orbitals (MOs) of the complexes (Figure 3) show that for both isomers, the net (C)S···S(C) bonding interaction originates from the overlap of the formally singly occupied MOs of the anionic radicals \([(\text{S})\text{C(Ph}_2\text{S)}_2]^-\), giving rise to the \(A_g\) symmetric bonding orbital of the \(C_{2h}\) symmetric complex. However, this overlap is considerably better for the structure with a \(C_1\) point group due to the symmetry allowed mixing of the individual p-type atomic orbitals (AOs) on sulfur. Consequently, as the overlap between the sulfur centered AOs is increased by lowering the symmetry, the overlap between the p-orbitals on sulfur atoms and the d-orbitals on the metal centers becomes polarized, resulting in an asymmetric bonding situation for the central \(E_2M_2\) unit. Figure 3 also shows that, because of asymmetry, there is another \(A_g\) symmetric orbital which is not strictly a (C)S···S(C) anti-bonding
orbital for the isomer with a $C_1$ point group, which yields an overall shortening of the key chalcogen-chalcogen interaction by 0.165 Å as compared to the $C_{2h}$ symmetric form. What is common to both isomers however is the composition of the relatively low-energy LUMO ($B_u/A_u$ symmetry) which can be readily identified as the anti-bonding counterpart of the dominant $A_g$ symmetric bonding orbital.

The above results seem to offer direct support for the structural flexibility of the $E_2M_2$ unit in compounds 5 and 6 as well as provide a rationale for the experimentally observed bonding trends. However, additional calculations performed for the phenyl substituted system 5c resulted in location of only the $C_1$ symmetric isomer on the PES. The optimized geometry of 5c is depicted in Figure 4 along with the key structural parameters, revealing a short (C)S···S(C) distance and a highly asymmetric bonding situation for the central $E_2M_2$ unit that differs considerably from either of the two independent molecules located in the crystal lattice (Figure 1). Hence, this finding provided sufficient incentive to perform geometry optimizations and electronic structure analyses for all systems 5 and 6 using density functional theory (DFT). As seen from Figure 4, the similarity of metrical parameters between optimized geometries and X-ray crystal structures ranges from good to excellent for 5a, 5b and 6b, leaving 5c as the only outcast in the series for which experimental data are available for comparison.

The non-existence of the $C_{2h}$ symmetric minimum in the potential energy surfaces of the phenyl derivatives 5 and 6 can easily be rationalized as a consequence of the steric bulk of substituents. Consequently, all optimizations employing symmetry constraints resulted in location of stationary points which were identified as transition states with respect to molecular symmetry breaking due to twisting of the aromatic rings. However, the discrepancies between the optimized and experimental structure of 5c necessitate a more in-depth analysis. The most straightforward explanation for the observed differences is the flatness of the PES with respect to changes in bonding within the $E_2M_2$ unit. This is supported not only by our theoretical results for the $R=H$
model system (5d), but also by the $^{31}$P$^{1}$H NMR spectrum of 5c in which a singlet is observed (no $^{2}J(^{31}$P,$^{31}$P) coupling) indicating equivalence in the Cu−S(C) bonds in contrast to the solid-state structure. Furthermore, 5c displays two independent molecules in the crystal lattice of which neither shows any major secondary bonding interactions that would account for the significant disparity in the (C)S···S(C) distances. On the other hand, the X-ray data of the (C)Se···Se(C) bonded compound 5b also displays two independent molecules,\cite{11} but in this case the theoretically predicted geometry is in good agreement with the averaged experimental bond parameters. Hence, the flatness of the PES with respect to changes in bonding within the E$_{2}$M$_{2}$ unit appears not to be the sole contributor to the poor performance of the chosen DFT approach in modeling the structure of 5c.

As noted earlier, the (C)S···S(C) distances in 5c are in the same range as the transannular S···S interactions in several sulfur-nitrogen heterocycles for which diradical character has been suggested but not theoretically confirmed.\cite{19} Consequently, it was of interest to investigate whether near-degeneracy effects play any role in the bonding of 5c which formally can be viewed as the Cu(I) coordinated dimer of the anionic radical [(S)C(PPh$_{2}$S)$_{2}$]$^{-}$. Unfortunately the molecular size prevents us from performing calculations with multiconfigurational methods (e.g. CAS-SCF) which are theoretically the most robust for the treatment of systems with possible diradical nature.\cite{27} Hence, we chose to adopt an indirect approach and performed additional geometry optimizations for 5c using the standard Hartree-Fock and second order Möller-Plesset perturbation theory (MP2) methods as well as employing the non-hybrid PBEPBE density functional. Typically, in cases in which diradical character plays a notable role, the sporadic performance of different computational approaches serves as a first indication of the underlying complexity in the wave function.\cite{27} For weak radical···radical interactions on the singlet PES, the restricted Hartree-Fock wave function is qualitatively incorrect and yields perfect pairing of electrons (i.e. a covalent bond) by construction. In contrast, the MP2 method gives exactly the opposite result as the pertubational approach overestimates the effects of electron correlation and consequently gives too much weight for the
excited determinant in the description. The performance of the different density functionals in modeling singlet states with diradical character is related not only to the identity of the functional but also to the amount of exact, Hartree-Fock exchange used in its construction.\[28\]

Calculations conducted for 5c at different theoretical levels give indirect support for diradical character in the ground state of this molecular complex. The Hartree-Fock optimized geometry shows a highly asymmetric S$_2$Cu$_2$ unit with a (C)S–S(C) distance very close to a single bond, 2.211 Å. In contrast, the MP2 minimum has an almost square-like S$_2$Cu$_2$ core with a (C)S···S(C) interaction that approaches the sum of van der Waals radii for two sulfur atoms, 3.60 Å. The PBEPBE optimized geometry is similar to the MP2 structure with a relatively long, 3.060 Å, (C)S···S(C) distance. Hence, the inclusion of 25% of exact exchange results in shortening of the key chalcogen···chalcogen interaction by as much as 0.70 Å! Clearly the geometry of the S$_2$Cu$_2$ unit in 5c is extremely sensitive to the chosen theoretical approach and, in particular, to the treatment of electron correlation effects. Additional support for the presence of diradical character in the wave function of 5c comes from the fact that Hartree-Fock even predicts the triplet PES of 5c to be lower in energy than the singlet. When using DFT, the singlet PES falls below the triplet and the restricted Kohn-Sham determinant has no internal instabilities giving rise to broken-symmetry solutions.

The above results enable us to conclude that the inability of the different theoretical methods to reproduce the crystal structure geometry of 5c can, in part, be related to the non-trivial nature of the (C)S···S(C) interaction. The restricted Hartree-Fock determinant yields perfect pairing of electrons, giving an exactly doubly occupied S···S bonding orbital (HOMO) and an empty low-energy S···S anti-bonding orbital (LUMO) (cf. orbitals in Figure 3). Consequently, the calculated HOMO-LUMO gap is as high as 9.6 eV. However, the configuration with a doubly occupied LUMO is close in energy to the Hartree-Fock minimum and should in the current case be included in the description. Natural orbitals calculated from the MP2 optimized wave function reveal that this is indeed what takes place, showing population of the Hartree-Fock LUMO by 0.15 electrons, but
the effect is overestimated due to the perturbational approximation. As a result, there is hardly any bonding interaction present, which also leads to significant decrease in the predicted HOMO-LUMO gap. In the case of DFT, diradical character is modeled primarily by the exchange-correlation functional and while 25% of exact exchange represents a good approximation for closed-shell molecules, it leads to slight underestimation of the diradical nature in 5c. Nevertheless, the presence of near-degeneracy effects can be clearly seen from the calculated HOMO-LUMO gap which is only 3.5 eV. Conversely, without any exact exchange, the PBEPBE functional yields two almost degenerate orbitals (a HOMO-LUMO gap of 0.8 eV!) giving virtually no bonding interaction between the two chalcogen centers. Although it is impossible to give a wave-function-based metric of diradical character in 5c without any data from multiconfigurational calculations, the amount is likely to be no more than 10% considering both the population of the MP2 natural orbitals and the fact that no broken-symmetry singlet solutions can be located for either of the employed density functionals. We also note that the singlet diradical character in 5c is related strictly to the sulfur atoms within the E₂M₂ unit. Hence, there appears to be no contribution to the overall wave function from electronic configurations involving Cu(II) atoms, cf. redox processes to afford Au(I)/Au(III) complexes 7b and 7c with two [(E)C(PPh₂S)₂]²⁻ counter-anions (E = S, Se) (vide supra).

An important question which now arises is the magnitude of the influence of diradical character on the electronic structures of the other investigated species 5 and 6. Again, all efforts to answer this question accurately are hampered by the size of the systems. Nevertheless, we chose to adopt an indirect method also in this case and compared the key metrical parameters from geometry optimizations using the PBEPBE and PBE1PBE density functionals. In the case of compounds 6b and 6c, the differences in the calculated bond lengths within the E₂M₂ unit (E = S, Se) are small (ca. 0.1 Å). However, for both 5a and 5b the (C)Se···Se(C) interaction changes as much as 0.4 Å in response to the variation in the amount of exact exchange used (cf. 0.7 Å for (C)S···S(C) in 5c). This
implies that the diradical character in 5 and 6 is dependent on the identity of the chalcogen atom within the E₂M₂ unit and significant only for systems which incorporate copper as the counterion.

Synthesis and X-ray structures of \{Au[(E)C(PPh₂S)]₂\}_2 (7b, E = Se; 7c, E = S). Metallophilic d^{10}-d^{10} closed shell interactions are well established for a wide variety of gold(I) complexes, but this phenomenon is still somewhat controversial for Cu(I) and Ag(I).[29, 30] With a view to the possible existence of aurophilic interactions in gold complexes of the dichalcogenide dianions 4b,c,[31] the reactions of Li₂4b and Li₂4c with Au(CO)Cl as the gold(I) source were carried out. In THF at -80 °C these reactions afforded dark red powders in 80% (7b) and 90% (7c) yields, respectively. The \(^{31}\text{P}\{\text{¹H}\} NMR spectra in CD₂Cl₂ displayed two well-separated broad singlets at δ 71.1 and 48.9 for 7b and two mutually coupled doublets at δ 68.5 and 44.8 with \(2\mathcal{J}(^{31}\text{P},^{31}\text{P}) = 54.0\) Hz for the all-sulfur derivative 7c.[33] The NMR spectroscopic data therefore indicated the formation of diamagnetic gold complexes (no significant paramagnetic shift) that are structurally different from the dinuclear copper and silver complexes, 5a-c and 6b,c, respectively.

Both 7b and 7c were identified in the solid state by single crystal X-ray structure determinations. The crystal structures of the CH₂Cl₂ solvates, \{Au[(E)C(PPh₂S)]₂(CH₂Cl₂)\}_2 [7b·(CH₂Cl₂)₂, E = Se; 7c·(CH₂Cl₂)₂, E = S], confirm the structural disparity between the gold complexes 7b,c and those of the lighter coinage metals. As illustrated in Figure 5, the central (C)E–E(C) bond (E = S, Se) of the dichalcogenide ligand has been cleaved resulting in a reduction of the ligand to generate two monomeric dianions 3b or 3c. Concomitantly, two distinct gold environments with approximately square-planar (four-coordinate) and linear (two-coordinate) metal centers have been created in the isostructural compounds 7b and 7c, consistent with the presence of Au(III) and Au(I), respectively.[34] Close inspection of the C–E bond lengths (E = S, Se) in 7b and 7c (Table 3) reveals a slight increase of ca. 0.03-0.05 Å compared to those in the binuclear Cu and Ag complexes 5a-c and 6b (ref. 11 and Table 2) consistent with the formation of the diamagnetic
dianions, [(E)C(PPh₂S)₂]²⁻ (3b, E = Se; 3c, E = S) rather than the corresponding radical anions, [(E)C(PPh₂S)₂]⁻, as was also inferred from the ³¹P NMR data. In summary, the two-electron reduction of the dimeric dichalcogenide ligands 4b or 4c to two equivalents of 3b or 3c is accompanied by the two-electron oxidation of one of the Au(I) centers to Au(III).

Several mixed oxidation state Au(I)/Au(III) complexes with metallophilic d¹⁰-d⁸ close contacts have been reported and theoretical studies on the nature of these interactions have been performed. Typically these compounds are constructed by interaction of Au(I) and Au(III) sources or by the (sometimes spontaneous) reduction of a Au(III)/Au(III) precursor. Although the oxidation of dinuclear gold(I) complexes generally results in the formation of Au(II)/Au(II) and, subsequently, Au(III)/Au(III) products, a number of reports indicate the spontaneous isomerization of Au(II)/Au(II) precursors into mixed oxidation state Au(I)/Au(III) complexes. A similar disproportionation process could lead to the formation of 7b and 7c from Au(II)/Au(II) complexes of 3b and 3c, respectively. In this context it is pertinent to note the connection between the proposed Au(II)/Au(II) precursors of 7b,c and the previously reported binuclear Hg(II) complex of the monomeric, all-selenium dianion 3a. In the latter case there is no driving force for the transformation of the Hg(II)/Hg(II) complex into the Hg(I)/Hg(III) isomer.

The calculated bond energies of 21-25 kJmol⁻¹ (at the MP2 level) for mixed oxidation state Au(I)…Au(III) aurophilic interactions are somewhat weaker than those of the corresponding Au(I)…Au(I) contacts. Consequently, intramolecular close contacts of 3.2-3.8 Å between the two metals are usually longer than typical Au(I)…Au(I) distances of 2.8-3.5 Å. Thus, the Au(I)…Au(III) connections of 3.125(1) and 3.119(1) Å (Table 3) observed in 7b and 7c, respectively, can be considered as relatively strong interactions. However, these values do fall within the range of 2.98-3.18 Å reported for close contacts between square-planar Au(III) and linear Au(I) in complexes in which the supporting ligands bring the two metal centers into close proximity possibly owing to steric hindrance. The S–Au(I)–S angles in both compounds are notably bent.
from linearity (by ca. 25°) consistent with a relatively strong Au(I)···Au(III) interaction in these complexes, cf. $\angle S$−Au(I)−S = 169.9(3)$^\circ$ in [Au$_2$(PhP(C$_6$H$_4$S)$_2$)$_2$] with an Au(I)···Au(III) distance of 2.978(2) Å.$^{[39]}$ The Au(III)−S bonds in 7b and 7c are expectedly ca. 0.05 and 0.10 Å shorter than the corresponding gold(I) contacts to the carbon- and phosphorus-bound sulfur atoms, respectively. The Au−Se distances of ca. 2.45 Å in 7b are similar to literature values,$^{[32a, 37c]}$ while the P−S bond lengths in both 7b and 7c exhibit a slight increase of ca. 0.03 Å compared to those in the copper and silver complexes 5 and 6. In contrast to complexes 5 and 6, the PCP-carbons in 7b and 7c show significant deviation from planarity $\Sigma \angle C = 341$-$345^\circ$, which are, however, consistent with the values observed in the group 12, 14 and 16 complexes of the dianion 3a, $\{M_n[(Se)C(PPh_2Se)_2]_2\}$ (n = 1, M = Sn, Te; n = 2, M = Hg).$^{[8]}$ The bond angles around the square planar Au(III) centers in 7b and 7c deviate from the ideal values by 2.5-$7.5^\circ$, and these chalcogen atoms lie in a plane approximately perpendicular to the Au(I) atom.

**UV-visible spectra of 5a-c, 6b,c and 7b,c.** Deeply colored CH$_2$Cl$_2$ solutions of the dinuclear copper complexes 5a-c absorb at significantly longer wavelengths (lower energies, 500-635 nm) compared to solutions of their silver analogues 6b,c (415-460 nm) (Figure 6a). Consequently, the strength of the (C)E−E(C) contacts is reflected in the energies of the observed electronic transitions: the weakest E−E contact in the all-sulfur derivative 5c (E = S) shows the lowest energy transition at 634 nm and the strongest E−E contact which is found in 6b (E = Se) results in an absorption signal at the highest energy at 459 nm (Se−Se bond length of 2.510(2) Å in the solid state), which may, however, be affected by isomerization (vide supra). By analogy, the absorption band at 413 nm seen for the all-sulfur complex 6c suggests a somewhat stronger (C)S−S(C) bond than the corresponding (C)Se−Se(C) contact in the selenium derivative 6b. It is also of note that the complexes 5a,b as well as 6b,c exhibit a single broadened band in the visible region, whereas the all-sulfur Cu(I)/Cu(I)
complex 5c displays two separate bands at very different wavelengths (423 and 634 nm) consistent with the intriguing greenish-blue color of the compound. The extinction coefficients of complexes 5a-c and 6b,c are in the narrow range of 3600-8200 M$^{-1}$cm$^{-1}$.

In order to characterize the transitions observed in the UV-visible spectra shown in Figure 6a, time-dependent density functional theory (TD-DFT) calculations were carried out for the optimized structures at the PBE1PBE/def-TZVP level of theory. Considering the results from electronic structure analyses of compounds 5 and 6, we expect the calculated spectra not to be fully in harmony with the experimental data throughout the series. First, the calculated geometries match the X-ray crystal data only in case of 5a, 5b and 6b. Furthermore, the silver complex 6b shows two singlets in its solution state $^{31}$P{$^1$H} NMR spectrum, possibly owing to isomerization, whereas only one singlet is observed for all 5a-c and 6c, indicating equivalence of all phosphorus atoms, most likely through a process by which the two energetically degenerate mirror images of the complexes interconvert. Hence, the geometries of the complexes are inevitably different in solution as compared to the crystal data, at least in the NMR timescale. Consequently, we anticipate the computational results to be semi-quantitative at best, but the analysis should nevertheless provide qualitative insight to the nature of the observed transitions.

Table 4 includes the theoretically predicted transition maxima for complexes 5a-c and 6b,c along with an orbital-based description of their dominant contributions. In general, there is only one principal (high-intensity) transition found for each molecule. The only exception to this is 5a, for which two equally intense transitions are predicted at 458 and 499 nm. Although there is no quantitative agreement between the theoretically predicted and experimental transition maxima, the TD-DFT method does in fact reproduce the qualitative trends if the data for 5c are excluded from the analysis. First, the calculated wavelengths show the expected dependence on the identity of both the chalcogen atom as well as the counterion. Second, the experimental UV-Visible spectrum of 5a shows a very broad band, in agreement with the theoretical prediction of two close-lying equal-
intensity transitions. Third, in addition to the principal transitions in Table 4, the calculations show that, for each of the studied complexes, there exists also a low-intensity high-wavelength band in the region 500-750 nm, which can be readily identified from the asymmetric line shape in the experimental spectra. In each of the complexes studied, this transition has a dominant contribution from the HOMO→LUMO excitation. Hence, it is not totally unexpected that 5c, with the most diradical character, shows a transition maximum in this area and that this feature is not reproduced by our calculations which also failed to describe the key interaction. It is anticipated that a more accurate treatment of diradical character would be needed in order to obtain a reasonable match between the experimental and theoretical electronic spectra for 5c. Such calculations are, unfortunately, far beyond the scope of the current computational resources available.

The dinuclear gold complexes 7b and 7c also form deeply colored solutions in CH₂Cl₂. The UV-visible spectra of both compounds feature three overlapping, yet distinct, absorption bands (Figure 6b). The lowest energy absorptions at ca. 651 (7b) and 634 nm (7c) may be attributed to the d → d transitions of the Au(I) and Au(III) centers, however their relatively high extinction coefficient values (~1500 and 2300 M⁻¹cm⁻¹ for 7b and 7c, respectively) are higher than typical values for these transitions. The remaining two absorption bands observed at virtually identical wavelengths for 7b and 7c (ca. 460 and 525 nm) are tentatively assigned to ligand-to-metal CT transitions. The extinction coefficient of the band at ca. 525 nm is almost double for the all-sulfur derivative 7c compared to 7b, while those of the high energy band (at 460 nm) are virtually identical. We have not attempted to calculate transition maxima for either 7b or 7c due to the difficulties associated with modeling aurophilic interactions with computational methods and DFT in particular.²⁹ᵃ,ᶜ

Conclusions
Completion of the series of binuclear Cu(I) complexes, \{Cu_2[(E'Ph_2P)_2CEEC(PPh_2E')_2]\} (5a, E = E' = Se;\[11\] 5b, E = Se, E' = S;\[11\] 5c, E = E' = S), with the generation of the all-sulfur derivative 5c reveals an intriguing trend in the stretching of the central (C)E−E(C) bond (E = S, Se). Although the Cu−E contacts (E = S, Se) in 5c are comparable with those in 5a and 5b, the elongation of the (C)E−E(C) interaction previously observed in the selenium congeners 5a and 5b (E = Se)\[11\] is more pronounced in the complex 5c (E = S). This results in a sufficient separation of the formal components of the dimeric ligand 4c, i.e. the radical anions [(S)C(PPh_2S)]\(-\), to afford some diradical character for the dinuclear complex as supported by theoretical calculations. The influence of this diradical character on the reactivity of 5c towards small molecules activation merits further investigations.\[40\] Copper-disulfide interactions are of significance in the context of redox or electron transfer processes in biological systems.\[15, 41, 42\] The disulfide → thiolate interconversion between RSSR and 2RS\(-\) on a distinct dicopper unit has been established for model systems\[43\] and disulfides have been used recently as an oxidant for Cu(I).\[15\] Complex 5c with a markedly elongated S−S bond coordinated to two copper centers may be considered as a model for the intermediates involved in oxidative-additions of disulfides to Cu(I). The diradical nature found for 5 and 6, and 5c in particular, also gives a strong incentive for carrying out electronic structure and wave function analyses for sulfur-nitrogen heterocycles such as S\(_4\)N\(_4\). Detailed theoretical investigations on this topic are currently being pursued.

The dinuclear Ag(I)/Ag(I) complex 6b exhibits an overall geometry similar to those of the Cu(I)/Cu(I) complexes 5a-c. The significantly weaker Ag⋯Se(C) contacts in 6b, however, result in a stronger (C)Se⋯Se(C) bond than that in the corresponding copper complexes in the solid state. The weak Ag⋯Se(C) contacts are also likely responsible for the fluxional behaviour revealed by VT NMR solution studies for 6b. The absence of similar behavior for the all-sulfur derivative 6c suggests somewhat stronger Ag⋯S(C) contacts.
In contrast to the formation of dinuclear Cu(I)/Cu(I) and Ag(I)/Ag(I) complexes in metathesis of the Li⁺ derivatives of the dimeric dianions 4b,c with M(I) reagents, the analogous reactions with Au(CO)Cl in a 1:2 molar ratio result in a redox transformation in which the ligands are reduced to afford two equivalents of the monomeric dianions 3b,c and one of the metals is oxidized to give a square-planar Au(III) center. The complexes 7b and 7c both exhibit a fairly strong intramolecular Au(I)···Au(III) interaction, which gives rise to markedly bent S–Au(I)–S units in the solid state.

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Experimental section

Reagents and general procedures

All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. The compounds [H₂C(PPh₂)₂] (Aldrich, 97%), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et₂O), CuCl (Aldrich, 99.995%), CuCl₂ (Aldrich, 99.995%), AgSO₃CF₃ (Strem Chemicals, 99%), and (OC)AuCl (Strem Chemicals, min. 97%) were used as received. [Li(TMEDA)]₂[(E)C(PPh₂S)₂] and [Li(TMEDA)]₂[(SPh₂P)₂CEEC(PPh₂S)₂] (E = S, Se) were prepared as reported earlier.¹⁰ The solvents n-hexane, toluene, Et₂O and THF were dried by distillation over Na/benzophenone and CH₂Cl₂ over CaH₂ under an argon atmosphere prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary. Although the values for C
analysis for the gold complexes 7b and 7c were 2-3 % low, these products were shown to be spectroscopically pure by NMR: $^{31}$P (no P-containing impurities) and $^7$Li (absence of LiCl by-product).

**Spectroscopic methods**

The $^1$H and $^{31}$P($^1$H) NMR spectra were obtained in CD$_2$Cl$_2$ at 23 °C on a Bruker DRX 400 spectrometer operating at 399.46 and 161.71 MHz, respectively. $^1$H NMR spectra are referenced to the solvent signal and the chemical shifts are reported relative to (CH$_3$)$_4$Si. The $^{31}$P($^1$H) NMR spectra are referenced externally and the chemical shifts are reported relative to an 85% solution of H$_3$PO$_4$.

**X-ray crystallography**

Crystallographic data for 5c, 6b, 7b and 7c are summarized in Table 1. Crystals of \{Cu$_2$[(SPh$_2$)$_2$CSSC(PPh$_2$S)$_2$]}·(CH$_2$Cl)$_2$ \[5c·(CH$_2$Cl)$_2]\], \{Ag$_2$[(SPh$_2$)$_2$CSeSeC(PPh$_2$S)$_2$]} \[6b\], \{Au[(Se)C(PPh$_2$S)$_2$](CH$_2$Cl)$_2$\}$_2$ \[7b·(CH$_2$Cl)$_2\]$_2$ and \{Au[(S)C(PPh$_2$S)$_2$](CH$_2$Cl)$_2$\}$_2$ \[7c·(CH$_2$Cl)$_2\]$_2$ were coated with Paratone 8277 oil and mounted on a glass fibre. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at -100 °C. The data sets were corrected for Lorentz and polarization effects, and empirical absorption correction was applied to the net intensities. Structures were solved by direct methods using SIR-92$^{[44]}$ and refined using SHELXL-97$^{[45]}$. After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C-H = 0.95 Å for -CH and 0.99 Å for -CH$_2$ hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for -CH and -CH$_2$ hydrogens. In the final refinement the hydrogen atoms were riding on their respective carbon atoms. CCDC817951-817954 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.

Computational Details

Theoretical calculations were performed for 5a-d and 6b,c. The structures of the complexes were fully optimized using a variety of computational methods including Hartree-Fock, second order Möller-Plesset perturbation theory (MP2) as well as PBEPBE and PBE1PBE density functionals.\[46\] Ahlrichs’ triple-zeta valence basis sets augmented by one set of polarization functions (def-TZVP) were used throughout the work.\[47\] The calculation of electronic transitions was conducted employing the time-dependent density functional theory formalism and the PBE1PBE exchange-correlation functional. All calculations were performed with the Gaussian 03\[48\] and Turbomole 6.1\[49\] program packages. Visualizations of frontier orbitals and molecular structures were done with gOpenMol.\[50\]

Spectroscopic data of \{Cu2[(SePh2P)2CSeC(PPh2Se)2]\} (5a).\[11\] 1H NMR (CD2Cl2, 23 °C): δ 7.00-7.57 [m, 40H, C6H5]; 31P{1H} NMR (CD2Cl2, 23 °C): δ 49.8 [s, 1J(31P,77Se) = 561 Hz, 2J(31P,31P) = 51.1 Hz]. UV-Vis (CH2Cl2): 563 nm (ε = 7.2 × 10^3 M⁻¹cm⁻¹).

Spectroscopic data of \{Cu2[(SPh2P)2CSeC(PPh2S)2]\} (5b).\[11\] 1H NMR (CD2Cl2, 23 °C): δ 7.01-7.48 [m, 40H, C6H5]; 31P{1H}: δ 59.5. UV-Vis (CH2Cl2): 497 nm (ε = 6.6 × 10^3 M⁻¹cm⁻¹).

Synthesis of \{Cu2[(SPh2P)2CSSC(PPh2S)2]\} (5c). Method A. A solution of [Li(TMEDA)]2[(S)C(PPh2S)2] (0.60 mmol, prepared in situ from 0.269 g of [H2C(PPh2S)2], 0.75 mL of MeLi, 0.139 g of TMEDA and 0.019 g of S8)\[10\] in toluene (20 mL) was added to a suspension of
CuCl$_2$ (0.081 g, 0.60 mmol) in toluene (5 mL) at -80 °C. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The resulting dark powder was allowed to settle and the solution was decanted via cannula. The product was washed with toluene (40 mL) affording {Cu$_2$[(SPh$_2$P)$_2$CSSC(PPh$_2$S)$_2$]} (5c) as a dark blue powder (0.192 g, 59%). Elemental analysis calcd (%) for C$_{50}$H$_{40}$Cu$_2$P$_4$S$_6$: C, 55.46; H, 3.73; found: C, 55.43; H, 3.94. $^1$H NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ 7.05-7.58 [m, 40H, C$_6$H$_5$]; $^{31}$P{$^1$H}: $\delta$ 59.6. UV-Vis (CH$_2$Cl$_2$): 423 nm ($\varepsilon = 3.6 \times 10^3$ M$^{-1}$cm$^{-1}$) and 634 nm ($\varepsilon = 5.0 \times 10^3$ M$^{-1}$cm$^{-1}$). $^{13}$C NMR spectrum could not be recorded due to poor solubility of the compound. X-ray quality crystals were obtained from the CH$_2$Cl$_2$ solution of 5c after 24 h at 23 °C.

**Method B.** A mixture of [Li(TMEDA)]$_2$[(SPh$_2$P)$_2$CSSC(PPh$_2$S)$_2$] (0.144 g, 0.12 mmol) and CuCl (0.024 g, 0.24 mmol) powders was cooled to -80 °C and cold THF (20 mL) was added via cannula. The reaction mixture was stirred for 15 min at -80 °C and 1 ½ h at 23 °C. The solvent was evaporated under vacuum, and the product was washed with Et$_2$O (30 mL) and toluene (30 mL) affording {Cu$_2$[(SPh$_2$P)$_2$CSSC(PPh$_2$S)$_2$]} (5c) as a dark blue powder (0.103 g, 79%). The identity of the product was confirmed by both NMR spectroscopy and X-ray crystallography (unit cell measurement after recrystallization from pentane/CH$_2$Cl$_2$ mixture).

**Synthesis of {Ag$_2$[(SPh$_2$P)$_2$CSeSeC(PPh$_2$S)$_2$]} (6b).** A mixture of [Li(TMEDA)]$_2$[(SPh$_2$P)$_2$CSeSeC(PPh$_2$S)$_2$] (0.259 g, 0.20 mmol) and AgOSO$_2$CF$_3$ (0.103 g, 0.40 mmol) powders was cooled to -80 °C and cold THF (20 mL) was added via cannula. The reaction mixture was stirred for 15 min at -80 °C and 1 ½ h at 23 °C resulting in a dark red solution. The solvent was evaporated under a vacuum and the product was washed with toluene (50 mL) affording {Ag$_2$[(SPh$_2$P)$_2$CSeSeC(PPh$_2$S)$_2$]} (6b) as a brownish red powder (0.235 g, 93%). Elemental analysis calcd (%) for C$_{50}$H$_{40}$Ag$_2$P$_4$S$_4$Se$_2$: C, 47.40; H, 3.18; found: C, 47.32; H, 3.25. $^1$H NMR (CD$_2$Cl$_2$, 23
°C): δ 7.05-7.97 [m, 40H, C₆H₅]; ³¹P{¹H}: δ 57.7 and 53.1 (23 °C, only δ 57.5 at -40 °C). UV-Vis (CH₂Cl₂): 459 nm (ε = 6.5 × 10³ M⁻¹cm⁻¹). ¹³C and ⁷⁷Se NMR spectra were not obtained due to poor solubility of the compound. X-ray quality crystals were obtained from the CH₂Cl₂ solution of 6b after 15 h at 23 °C.

**Synthesis of {Ag₂[(SPh₂P)₂CSSC(PPh₂S)₂]} (6c).** A mixture of [Li(TMEDA)]₂[(SPh₂P)₂CSSC(PPh₂S)₂] (0.144 g, 0.12 mmol) and AgOSO₂CF₃ (0.062 g, 0.24 mmol) powders was cooled to -80 °C and cold THF (20 mL) was added via cannula. The reaction mixture was stirred for 15 min at -80 °C and 1 ½ h at 23 °C resulting in an orange powder and pale yellow solution. The precipitate was allowed to settle and the solution was decanted via a cannula. The product was washed with Et₂O (30 mL) affording {Ag₂[(SPh₂P)₂CSSC(PPh₂S)₂]} (6c) as an orange powder (0.118 g, 84%). Elemental analysis calcd (%) for C₅₀H₄₀Ag₂P₄S₆: C, 51.29; H, 3.45; found: C, 51.30; H, 3.63. ¹H NMR (CD₂Cl₂, 23 °C): δ 7.07-7.53 [m, 40H, C₆H₅]; ³¹P{¹H}: δ 56.5. UV-Vis (CH₂Cl₂): 413 nm (ε = 8.2 × 10³ M⁻¹cm⁻¹). ¹³C NMR spectrum was not obtained due to poor solubility of the compound.

**Synthesis of {Au[(Se)C(PPh₂S)₂]}₂ (7b).** A mixture of [Li(TMEDA)]₂[(SPh₂P)₂CSeSeC(PPh₂S)₂] (0.261 g, 0.20 mmol) and (OC)AuCl (0.105 g, 0.40 mmol) powders was cooled to -80 °C and cold THF (20 mL) was added via cannula. The reaction mixture was stirred for 15 min at -80 °C and 1 ½ h at 23 °C resulting in a red solution and brownish-red precipitate. The solvent was evaporated under a vacuum and the product was washed with Et₂O (50 mL) affording {Au[(Se)C(PPh₂S)₂]}₂ (7b) as a dark red powder (0.232 g, 80%). ¹H NMR (CD₂Cl₂, 0 °C): δ 6.98-8.20 [m, 40H, C₆H₅]; ³¹P{¹H}: δ 71.1 (s, br) and 48.9 (s, br). UV-Vis (CH₂Cl₂): 458 nm (ε = 6.9 × 10³ M⁻¹cm⁻¹), 523 nm (ε = 4.7 × 10³ M⁻¹cm⁻¹) and 651 nm (ε = 1.5 × 10³ M⁻¹cm⁻¹). ¹³C and ⁷⁷Se NMR spectra were not obtained.
due to poor solubility of the compound. X-ray quality crystals were obtained by layering Et₂O on top of CH₂Cl₂ solution of 7b after 10 h at 5 ℃.

**Synthesis of {Au[(S)C(PPh₂S)₂]}₂ (7c).** A mixture of [Li(TMEDA)]₂[(SPh₂P)₂CSSC(PPh₂S)₂] (0.120 g, 0.10 mmol) and (OC)AuCl (0.052 g, 0.20 mmol) powders was cooled to -80 ℃ and cold THF (20 mL) was added via cannula. The reaction mixture was stirred for 15 min at -80 ℃ and 1 ½ h at 23 ℃ resulting in a dark red solution. The solvent was evaporated under a vacuum and the product was washed with Et₂O (50 mL) affording {Au[(S)C(PPh₂S)₂]}₂ (7c) as a dark red powder (0.122 g, 90%). ¹H NMR (CD₂Cl₂, 23 ℃): δ 6.89-8.19 [m, 40H, C₆H₅]; ³¹P{¹H}: δ 68.5 [d, 2J(³¹P, ³¹P) = 54.0 Hz] and 44.8 [d, 2J(³¹P, ³¹P) = 53.9 Hz]. UV-Vis (CH₂Cl₂): 457 nm (ε = 6.3 × 10³ M⁻¹cm⁻¹), 526 nm (ε = 8.7 × 10³ M⁻¹cm⁻¹) and 634 nm with ε = 2.3 × 10³ M⁻¹cm⁻¹. ¹³C NMR spectrum was not obtained due to poor solubility of the compound. X-ray quality crystals were obtained from a CH₂Cl₂ solution of 7c after 12 h at 23 ℃.

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Rearrangement of 6b to form an isomer in which the two Ag$^+$ ions are S,S'-chelated at the termini of the dimeric ligand, cf. [(TMEDA)Li]$_2$4b,[10] and, in particular, reversion to 6b upon cooling seems unlikely on the basis of energetic considerations.

Information on M···M close contacts to corroborate the stabilization of complexes by ligand-unsupported M···M connections (M = Cu, Ag) analogously to aurophilic interactions is still limited and has been a subject of several experimental and theoretical investigations.[31,32]
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Table 1. Crystallographic data for \{Cu_2[(SPh_2)P_CSSC(PPh_2)S_2](CH_2Cl_2)_2\} [5c\,(CH_2Cl_2)_2], \{Ag_2[(SPh_2)P_CSeSeC(PPh_2)S_2]\} (6b), \{Au[(Se)C(PPh_2)S_2](CH_2Cl_2)_2\} [7b\,(CH_2Cl_2)_2] and \{Au[(S)C(PPh_2)S_2](CH_2Cl_2)_2\} [7c\,(CH_2Cl_2)_2].

|       | 5c                     | 6b                     | 7b                     | 7c                     |
|-------|------------------------|------------------------|------------------------|------------------------|
| emp. formula | C_{52}H_{44}Cl_{4}Cu_{2}P_{4}S_{6} | C_{50}H_{40}Ag_{2}P_{4}S_{4}Se_{2} | C_{52}H_{44}Au_{2}Cl_{4}P_{4}S_{4}Se_{2} | C_{52}H_{44}Au_{2}Cl_{4}P_{4}S_{6} |
| Fw    | 1253.99                | 1266.60                | 1614.65                | 1520.84                |
| cryst. system | Triclinic              | Monoclinic             | Triclinic              | Triclinic              |
| space group | P-1                    | P2_1/n                 | P-1                    | P-1                    |
| a, Å  | 10.500(2)              | 10.534(2)              | 11.141(2)              | 11.129(2)              |
| b, Å  | 10.960(2)              | 18.142(4)              | 15.748(3)              | 15.715(3)              |
| c, Å  | 24.832(5)              | 13.075(3)              | 17.481(4)              | 17.430(4)              |
| α, deg. | 89.57(3)               | 90.00                  | 79.81(3)               | 79.81(3)               |
| β, deg. | 78.12(3)               | 107.58(3)              | 72.25(3)               | 72.21(3)               |
| γ, deg. | 72.95(3)               | 90.00                  | 72.15(3)               | 72.09(3)               |
| V, Å³ | 2669.3(9)              | 2382(1)                | 2769(1)                | 2750(1)                |
| Z     | 2                      | 2                      | 2                      | 2                      |
| T, °C | -100                   | -100                   | -100                   | -100                   |
| ρ\_calc, g/cm³ | 1.560                  | 1.766                  | 1.937                  | 1.836                  |
| μ(Mo Kα), mm⁻¹ | 1.388                  | 2.696                  | 7.103                  | 5.902                  |
| crystal size, mm³ | 0.12×0.10×0.06        | 0.08×0.06×0.02         | 0.10×0.08×0.02         | 0.10×0.08×0.02         |
| F(000) | 1276                  | 1252                  | 1548                  | 1476                  |
| Θ range, deg | 2.08-25.03             | 2.19-25.03             | 2.79-25.03             | 2.80-25.03             |
| Description                        | Value 1 | Value 2 | Value 3 | Value 4 |
|-----------------------------------|---------|---------|---------|---------|
| reflns collected                  | 16899   | 15354   | 18116   | 18150   |
| unique reflns                     | 9264    | 4204    | 9696    | 9578    |
| $R_{int}$                         | 0.0605  | 0.1020  | 0.0693  | 0.0509  |
| reflns [$I>2\sigma(I)$]           | 6941    | 3235    | 7352    | 7857    |
| $R_1$ [$I>2\sigma(I)$]           | 0.0740  | 0.0564  | 0.0635  | 0.0525  |
| $wR_2$ (all data)                 | 0.1538  | 0.1085  | 0.1385  | 0.1242  |
| GOF on $F^2$                      | 1.084   | 1.095   | 1.040   | 1.032   |
| completeness                      | 0.981   | 0.998   | 0.991   | 0.984   |

$a \lambda$ (MoKα) = 0.71073 Å.  
$b$ $R_1 = \Sigma |F_o| - |F_c| /\Sigma |F_o|$.  
$c$ $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. 
Table 2. Selected bond lengths (Å) and angles (°) in \([\text{Cu}_2(\text{SP}_{2} \text{P})_2 \text{CSSC}(\text{PP}S)_2] (\text{CH}_2\text{Cl})_2\) [5c](CH_2Cl_2) and [\text{Ag}_2(\text{SP}_{2} \text{P})_2 \text{CSeSeC}(\text{PP}S)_2]] (6b).

| Bond          | Length  | Angle   | Bond          | Length  | Angle   |
|---------------|---------|---------|---------------|---------|---------|
| S5⋯S5         | 2.540(4)| Cu1-S5  | 2.535(2)      | C1-P1   | 1.759(6)|
| Cu1-S1        | 2.230(2)| Cu1-S5a | 2.361(2)      | C1-P2   | 1.775(7)|
| Cu1-S2        | 2.236(2)| C1-S5   | 1.702(6)      | P1-S1   | 2.010(2)|
|               |         |         |               | P2-S2   |         | 2.001(2)|
| S1-Cu1-S5     | 97.80(7)| Cu1-S5-C1| 96.9(2)      | P2-C1-S5| 120.5(4)|
| S1-Cu1-S5a    | 126.71(7)| Cu1-S1-P1| 97.20(9)    | P1-C1-P2| 127.0(3)|
| S1-Cu1-S2a    | 127.96(8)| Cu1a-S2-P2| 98.28(9)   | C1-P1-S1| 114.1(2)|
| Cu1-S5-Cu1a   | 117.62(8)| P1-C1-S5| 112.5(4)    | C1-P2-S2| 111.5(2)|

5c (molecule B)

| Bond          | Length  | Angle   | Bond          | Length  | Angle   |
|---------------|---------|---------|---------------|---------|---------|
| S6⋯S6         | 2.720(3)| Cu2-S6  | 2.284(2)      | C2-P3   | 1.782(7)|
| Cu2-S3        | 2.257(2)| Cu2-S6b | 2.529(2)      | C2-P4   | 1.769(6)|
| Cu2-S4b       | 2.240(2)| C2-S6   | 1.705(6)      | P3-S3   | 2.000(2)|
|               |         |         |               | P4-S4   |         | 2.018(2)|
| S3-Cu2-S6     | 96.74(7)| Cu2-S6-C2| 104.2(2)    | P4-C2-S6| 109.8(3)|
| S3-Cu2-S6b    | 127.58(7)| Cu2-S3-P3| 99.56(9)   | P3-C2-P4| 128.8(4)|
| S3-Cu2-S4b    | 127.63(8)| Cu2b-S4-P4| 95.42(9)  | C2-P3-S3| 111.1(2)|
| Cu2-S6-Cu2b   | 111.39(8)| P3-C2-S6| 120.2(4)    | C2-P4-S4| 113.5(2)|

6b

| Bond          | Length  | Angle   | Bond          | Length  | Angle   |
|---------------|---------|---------|---------------|---------|---------|
| Se1-Se1       | 2.510(2)| Ag1-Se1 | 2.856(1)      | C1-P1   | 1.755(7)|
| Ag1-S1        | 2.420(2)| Ag1-Se1c| 3.200(1)     | C1-P2   | 1.739(7)|
| Ag1-S2c       | 2.400(2)| C1-Se1  | 1.888(7)      | P1-S1   | 2.016(3)|
|               |         |         |               | P2-S2   |         | 2.031(3)|
| S1-Ag1-Se1    | 86.75(5)| Ag1-Se1-C1| 99.4(2)     | P2-C1-Se1| 109.5(3)|
| S1-Ag1-Se1c   | 109.9(2)| Ag1-S1-P1| 98.08(9)    | P1-C1-P2| 132.8(4)|
| S1-Ag1-S2c    | 161.46(7)| Ag1c-S2-P2| 100.37(9) | C1-P1-S1| 113.8(3)|
| Ag1-Se1-Ag1c  | 131.4(3)| P1-C1-Se1| 115.5(4)     | C1-P2-S2| 119.0(3)|

Symmetry operations: \(^a\) 1-x, -y, 2-z, \(^b\) 2-x, -y, 1-z, \(^c\) -x, -y, 2-z.
Table 3. Selected bond lengths (Å) and angles (°) in $[\text{Au}[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]\cdot(\text{CH}_2\text{Cl}_2)]_2 [7\text{b}(\text{CH}_2\text{Cl}_2)_2]$ and $[\text{Au}[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]\cdot(\text{CH}_2\text{Cl}_2)]_2 [7\text{c}(\text{CH}_2\text{Cl}_2)_2]$.

|        | $7\text{b}$           | $7\text{c}$           | $7\text{b}$           | $7\text{c}$           |
|--------|-----------------------|-----------------------|-----------------------|-----------------------|
|        | $\text{Au}1\cdots\text{Au}2$ |                       | $\text{C}2\cdots\text{S}6$ | $1.907(14)^a$         | $1.754(9)$           |
|        | $\text{Au}1$--$\text{S}1$ | $2.419(3)$            | $\text{C}1$--$\text{P}1$ | $1.751(14)$           | $1.730(9)$           |
|        | $\text{Au}1$--$\text{S}3$ | $2.395(3)$            | $\text{C}1$--$\text{P}2$ | $1.741(13)$           | $1.746(9)$           |
|        | $\text{Au}1$--$\text{S}5$ | $2.441(2)^a$          | $\text{C}2$--$\text{P}3$ | $1.733(14)$           | $1.732(9)$           |
|        | $\text{Au}1$--$\text{S}6$ | $2.451(2)^a$          | $\text{C}2$--$\text{P}4$ | $1.731(13)$           | $1.753(9)$           |
|        | $\text{Au}2$--$\text{S}2$ | $2.289(3)$            | $\text{P}1$--$\text{S}1$ | $2.039(5)$            | $2.047(4)$           |
|        | $\text{Au}2$--$\text{S}4$ | $2.295(3)$            | $\text{P}2$--$\text{S}2$ | $2.035(5)$            | $2.029(3)$           |
|        | $\text{C}1$--$\text{S}5$ | $1.917(13)^a$         | $\text{P}3$--$\text{S}3$ | $2.057(5)$            | $2.048(3)$           |
|        |                       |                       | $\text{P}4$--$\text{S}4$ | $2.034(4)$            | $2.039(4)$           |
| $\text{S}1$--$\text{Au}1$--$\text{S}3$ | $88.4(1)$             | $86.86(8)$            | $\text{Au}1$--$\text{S}3$--$\text{P}3$ | $97.6(2)$            | $97.3(1)$           |
| $\text{S}1$--$\text{Au}1$--$\text{S}5$ | $93.24(9)^a$          | $94.18(8)$            | $\text{Au}1$--$\text{S}5$--$\text{C}1$ | $101.3(4)^a$         | $104.1(3)$           |
| $\text{S}1$--$\text{Au}1$--$\text{S}6$ | $175.64(8)^a$         | $172.72(9)$           | $\text{Au}1$--$\text{S}6$--$\text{C}2$ | $101.3(4)^a$         | $104.3(3)$           |
| $\text{S}3$--$\text{Au}1$--$\text{S}5$ | $172.63(9)^a$         | $178.59(8)$           | $\text{Au}2$--$\text{S}2$--$\text{P}2$ | $110.5(2)$           | $106.5(1)$           |
| $\text{S}3$--$\text{Au}1$--$\text{S}6$ | $95.29(8)^a$          | $92.76(8)$            | $\text{Au}2$--$\text{S}4$--$\text{P}4$ | $106.4(2)$           | $108.6(1)$           |
| $\text{S}5$--$\text{Au}1$--$\text{S}6$ | $83.43(2)^a$          | $86.33(8)$            | $\text{C}1$--$\text{P}1$--$\text{S}1$ | $115.4(2)$           | $110.9(3)$           |
| $\text{S}1$--$\text{Au}1$--$\text{Au}2$ | $91.45(8)$            | $92.37(7)$            | $\text{C}1$--$\text{P}2$--$\text{S}2$ | $120.5(5)$           | $117.7(3)$           |
| $\text{S}3$--$\text{Au}1$--$\text{Au}2$ | $90.54(9)$            | $91.48(7)$            | $\text{C}2$--$\text{P}3$--$\text{S}3$ | $113.1(5)$           | $112.7(3)$           |
| $\text{S}5$--$\text{Au}1$--$\text{Au}2$ | $96.61(5)^a$          | $87.53(7)$            | $\text{C}2$--$\text{P}4$--$\text{S}4$ | $118.5(4)$           | $119.0(3)$           |
| $\text{S}6$--$\text{Au}1$--$\text{Au}2$ | $86.14(4)^a$          | $94.90(7)$            | $\text{P}1$--$\text{C}1$--$\text{S}5$ | $104.9(7)^a$         | $109.0(5)$           |
| $\text{S}2$--$\text{Au}2$--$\text{S}4$ | $155.3(1)$            | $156.69(9)$           | $\text{P}2$--$\text{C}1$--$\text{S}5$ | $114.6(7)^a$         | $115.5(5)$           |
| $\text{S}2$--$\text{Au}2$--$\text{Au}1$ | $100.86(9)$           | $99.48(7)$            | $\text{P}3$--$\text{C}2$--$\text{S}6$ | $107.2(7)^a$         | $107.4(5)$           |
| $\text{S}4$--$\text{Au}2$--$\text{Au}1$ | $100.87(9)$           | $101.57(7)$           | $\text{P}4$--$\text{C}2$--$\text{S}6$ | $114.0(8)^a$         | $115.2(5)$           |
| $\text{Au}1$--$\text{S}1$--$\text{P}1$ | $98.9(2)$             | $96.6(1)$             | $\text{P}1$--$\text{C}1$--$\text{P}2$ | $121.4(7)$           | $120.2(5)$           |
|        |                       |                       | $\text{P}3$--$\text{C}2$--$\text{P}4$ | $120.8(8)$           | $122.4(5)$           |

$^a$ $\text{S}5 = \text{Se}1$, $\text{S}6 = \text{Se}2$. 
Table 4. Calculated (TD-PBE1PBE/def-TZVP) transition maxima for 5a-c and 6b,c in the visible region.

| complex | $\lambda_{\text{max}}$ (nm) | dominant contributions |
|---------|-----------------|-----------------------|
| 5a      | 499             | HOMO-1→LUMO (76%) HOMO-3→LUMO (19%) |
|         | 458             | HOMO-3→LUMO (78%) HOMO-1→LUMO (17%) |
| 5b      | 435             | HOMO-2→LUMO (87%)     |
| 5c      | 383             | HOMO-2→LUMO (73%) HOMO→LUMO+2 (9%)  |
| 6b      | 396             | HOMO-1→LUMO (74%) HOMO→LUMO (13%)  |
| 6c      | 374             | HOMO-1→LUMO (51%) HOMO→LUMO (17%)  HOMO→LUMO+2 (17%) HOMO→LUMO+4 (9%) |
Figure and Scheme Captions

Figure 1. Two independent molecules in the crystal structure of \( \text{Cu}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2 \) \[5c\cdot(\text{CH}_2\text{Cl}_2)_2\] with the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Symmetry operations: (A) 1-\(x\), -\(y\), 2-\(z\) and (B) 2-\(x\), -\(y\), 1-\(z\).

Figure 2. Molecular structure of \( \text{Ag}_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2] \) \(6b\) with the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Symmetry operation: -\(x\), -\(y\), 2-\(z\).

Figure 3. Frontier molecular orbitals of (a) \( C_{2h} \) and (b) \( C_i \) symmetric forms of \( \text{Cu}_2[(\text{SH}_2\text{P})_2\text{CSSC}(\text{PH}_2\text{S})_2] \) (orbital occupancies in parenthesis).

Figure 4. Optimized (PBE1PBE/def-TZVP) geometries of (a) \( 5a \), (b) \( 5b \), (c) \( 5c \), (d) \( 6b \) and (e) \( 6c \).

Figure 5. Crystal structures of (a) \( \text{Au}[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2 \) \[7b\cdot(\text{CH}_2\text{Cl}_2)_2\] and (b) \( \text{Au}[(\text{S})\text{C}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2 \) \[7c\cdot(\text{CH}_2\text{Cl}_2)_2\] with the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

Figure 6. Visible spectra of (a) \( 5a \) (\( \text{Cu}_2\text{Se}_6 \)), \( 5b \) (\( \text{Cu}_2\text{S}_4\text{Se}_2 \)), \( 5c \) (\( \text{Cu}_2\text{S}_6 \)), \( 6b \) (\( \text{Ag}_2\text{S}_4\text{Se}_2 \)) and \( 6c \) (\( \text{Ag}_2\text{S}_6 \)), and (b) \( 7b \) (\( \text{Au}_2\text{S}_4\text{Se}_2 \)) and \( 7c \) (\( \text{Au}_2\text{S}_6 \)) measured in \( \text{CH}_2\text{Cl}_2 \).

Scheme 1. Syntheses of the complexes \( 5c \), \( 6b,c \) and \( 7b,c \).
Scheme 2. Possible isomerization of compound 6b in solution.