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Bond Stretching and Redox Behavior in Coinage Metal Complexes of the Dichalcogenide Dianions $[(SPh_2P)_2CEEC(PPh_2S)_2]^{2-}$ (E = S, Se): Diradical Character of the Dinuclear Copper(I) Complex (E = S)

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Abstract: The metathetical reactions of (a) $[\text{Li}(\text{TMEDA})]_2[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]$ (**Li₂3c**) with CuCl_2 and (b) $[\text{Li}(\text{TMEDA})]_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]$ (**Li₂4c**) with two equivalents of CuCl both afford the binuclear Cu(I) complex $\{\text{Cu}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]\}$ (**5c**). The elongated (C)S–S(C) bond (ca. 2.54 and 2.72 Å) of the dianionic ligand observed in the solid-state structure of **5c** indicate the presence of diradical character as supported by theoretical analyses. The treatment of $[\text{Li}(\text{TMEDA})]_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2]$ (**Li₂4b**) and **Li₂4c** with $\text{AgOSO}_2\text{CF}_3$ produce the analogous Ag(I) derivatives, $\{\text{Ag}_2[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S})_2]\}$ (**6b**, E = Se; **6c**, E = S), respectively. The diselenide complex **6b** exhibits notably weaker Ag–Se(C) bonds than the corresponding contacts in the Cu(I) congeners, and the ^{31}P NMR data suggest a possible isomerization in solution. In contrast to the metathesis observed for Cu(I) and Ag(I) reagents, the reactions of **Li₂4b** and **Li₂4c** with $\text{Au}(\text{CO})\text{Cl}$ involve a redox process in which the dimeric dichalcogenide ligands are reduced to the corresponding monomeric dianions, $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**3b**, E = Se; **3c**, E = S), and one of the gold centers is oxidized to generate the mixed-valent Au(I)/Au(III) complexes, $\{\text{Au}[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]\}_2$ (**7b**, E = Se; **7c**, E = S), with relatively strong aurophilic Au(I)⋯Au(III) interactions. The new compounds **5c**, **6b,c** and **7b,c** are characterized in solution by NMR spectroscopy and in the solid state by X-ray crystallography (**5c**, **6b**, **7b** and **7c**) and by Raman spectroscopy (**5c** and **6c**). The UV-Visible spectra of coinage metal complexes of the type **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, $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**1**), by Le Floch and co-workers has opened the way for wide-ranging investigations of this intriguing dithio PCP-bridged ligand.^[1] A variety of complexes with main group^[2] and transition metals,^[1,3] as well as with lanthanides^[4] and actinides^[5] have revealed strong metal-carbon interactions. In addition, the mild oxidation of the dianion **1** with C_2Cl_6 or I_2 produced stable, monomeric or dimeric carbenoids, or a novel six-membered $\text{C}_2\text{P}_2\text{S}_2$ ring in $[(\text{SPh}_2\text{P})_2\text{C}_2(\text{PPh}_2)_2\text{S}_2]$ via a $\text{P} \rightarrow \text{C}$ *sulfur-transfer* process.^[6] Similarly, our recent investigations of the isoelectronic, diseleno monoanion, $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ (**2**), disclosed unusual carbon-centered reactivity. While the metathetical reactions of $[\text{Li}(\text{TMEDA})]\mathbf{2}$ with $\text{M}(\text{II})\text{Cl}_2$ ($\text{M} = \text{Zn}, \text{Hg}$) afforded the expected homoleptic group 12 complexes with *Se, Se'*-chelated ligands,^[7] 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 $\text{M}(\text{IV})$ complexes of the novel triseleno dianion $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$ (**3a**).^[8] In a related transformation, mild thermolysis of the mononuclear $\text{Hg}(\text{II})$ derivative of **2**, $\text{Hg}[\text{HC}(\text{PPh}_2\text{Se})_2]_2$, produced a dinuclear $\text{Hg}(\text{II})$ complex of **3a**,^[8] while monomeric $\text{Pb}(\text{II})$ complexes of **3b** and **3c** have been attained by chalcogen insertion into the $\text{Pb}-\text{C}$ bond of dimeric $\text{Pb}(\text{II})$ complexes of **1**.^[2a] Intriguingly, the reaction of dithio analogue of the monoanion **2**, $[\text{Li}(\text{THF})(\text{Et}_2\text{O})][\text{HC}(\text{PPh}_2\text{S})_2]$, with group 13 halides MCl_3 ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) in a 2:1 molar ratio produced the dianion **1** as the *S, C, S*-bonded dimers $[\text{MCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ via a process that probably involves metathesis followed by dehydrochlorination by the second equivalent of the lithium reagent.^[9]

These fascinating and structurally diverse complexes prompted us to design a direct synthesis of the novel trichalcogeno dianions, $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**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.^[10] The all-selenium derivative **3a** cannot be obtained via this route because of the unavailability of $\text{Li}_2[\text{C}(\text{PPh}_2\text{Se})_2]$ owing to cleavage

of P-Se bonds by RLi reagents.^[7] Our investigations of the one-electron oxidation of **3b,c** generated the novel dichalcogenides, [(SPh₂P)₂CEEC(PPh₂S)₂]²⁻ (**4b**, E = Se; **4c**, E = S), which are formally dimers of the corresponding radical anions [(E)C(PPh₂S)₂]^{•-} with moderately elongated (by ca. 8 %) central chalcogen-chalcogen bonds.^[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 CuCl₂ via proton-selenium exchange *and* a redox process (**5a**), (b) the redox reaction of the monomeric dianion **3b** with CuCl₂ (**5b**), and (c) metathesis of dimeric dianion **4b** with CuCl (**5b**).^[11] The η^2, η^2 -Se₂ bonding motif established for complexes **5a** and **5b** represents a new coordination mode for generic RSe–SeR ligands.^[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.^[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.^[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,^[14] therefore simulating, for example, biologically significant compounds with copper-disulfide interactions.^[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.^[13a] 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,^[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 {Cu₂[η^2, η^2 -(SPh₂P)₂CSSC(PPh₂S)₂]} (**5c**), the dinuclear Ag(I)/Ag(I) complexes {Ag₂[η^2, η^2 -(SPh₂P)₂CEEC(PPh₂S)₂]} (**6b**, E = Se; **6c**, E = S) and

the mixed oxidation state Au(I)/Au(III) complexes $\{\text{Au}[\text{S},\text{S}'\text{-(E)C}(\text{PPh}_2\text{S})_2]\text{Au}[\text{E},\text{E}',\text{S},\text{S}'\text{-(E)C}(\text{PPh}_2\text{S})_2]\}$ (**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 ^{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 $\{\text{Cu}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]\}$ (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).^[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, $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^{-\bullet}$? With this in mind, the reactions between (a) the monomeric dianion **3c** and $\text{Cu}(\text{II})\text{Cl}_2$ and (b) the dimeric dianion **4c** with two-equivalents of $\text{Cu}(\text{I})\text{Cl}$ were carried out (Scheme 1). As in the case of the selenium-containing systems,¹¹ the reactions proceeded cleanly at $-80\text{ }^\circ\text{C}$ to afford a dark blue powder in good yields. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product from both reactions displayed a singlet at 59.6 ppm, cf. δ 59.5 for **5b**,^[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_2Cl_2 solution. The structural determination confirmed the identity of this product as $\{\text{Cu}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]\}$ (**5c**), which crystallized as the CH_2Cl_2 solvate

[**5c**·(CH₂Cl₂)₂] isostructural with the selenium-containing congeners **5a** and **5b**.^[11] 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)]₂**4c**, thus indicating the presence of the dimeric dianion **4c** in the all-sulfur Cu(I) complex **5c**.^[10, 11] 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**,^[10] 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^[16] and values of 2.43–2.55 Å for the bicyclic compounds 1,5-R₄P₂N₄S₂ (R = alkyl, aryl),^[17, 18] for which diradical character has been suggested.^[19] 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,^[20] while the S–S separation in the trigonal bipyramidal trication [(tmedaCu)₃S₂]³⁺ is 2.73 Å.^[21–23]

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.^[11] 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 {Ag₂[(SPh₂P)₂CEEC(PPh₂S)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 AgOSO₂CF₃ 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 CH₂Cl₂ 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 {Ag₂[(SPh₂P)₂CSeSeC(PPh₂S)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 $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$, in which the metal cations are *S,S'*-chelated by each terminus of the dianionic ligand $\mathbf{4b}$.^[10]

In contrast to the copper complexes $\mathbf{5a-c}$ and to the all-sulfur silver complex $\mathbf{6c}$, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the selenium derivative $\mathbf{6b}$ in CD_2Cl_2 displays *two singlets* at δ 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 δ 56.5 for the sulfur congener $\mathbf{6c}$ and it also resembles the value of ca. δ 59.5 found for the copper complexes $\mathbf{5b}$ and $\mathbf{5c}$,^[11] while the high-field singlet approaches the chemical shift of ca. δ 50.5 reported for the dilithium derivatives $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$.^[10] When the solution of $\mathbf{6b}$ is cooled, the resonance at δ 53.1 gradually disappears and at -40 °C only the slightly shifted singlet at δ 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) $\text{Ag}\cdots\text{Se}(\text{C})$ distances in the solid-state structure of $\mathbf{6b}$ (Table 2) hint at two plausible explanations for the two singlets seen at room temperature. In the first proposal the two weakest silver \cdots selenium contacts ($\text{Ag}1\cdots\text{Se}1\text{A}$ and $\text{Ag}1\text{A}\cdots\text{Se}1$ in Figure 2) are cleaved in solution to afford a tetracyclic compound $\mathbf{6b}'$ (Scheme 2) with inequivalent phosphorus atoms as a part of five- and six-membered rings, respectively. However, the inequivalent phosphorus atoms of a $-\text{Ph}_2\text{PCPPH}_2-$ 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 $\mathbf{6b}$ despite the relatively narrow signals (half-width of ca. 40 Hz at 23 °C). In addition, the steady disappearance of the singlet at δ 53.1 when temperature is lowered is inconsistent with the presence of isomer $\mathbf{6b}'$, which would be expected to persist at lower temperatures.

An alternative explanation of the variable temperature NMR data involves the disruption of all four $\text{Ag}\cdots\text{Se}(\text{C})$ contacts in $\mathbf{6b}$ to give $\mathbf{6b}''$ (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 $\mu\text{-}\eta^2\text{;}\eta^2\text{-Se}_2$ coordination observed for **6b** in the solid state becomes symmetrical in solution so that only one ^{31}P resonance at δ 57.5 is observed, cf. similar behavior in the Cu(I) complexes **5a-c**.

The close proximity of the singlet at δ 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 $\text{Ag}\cdots\text{S}(\text{C})$ 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 $\text{S}\cdots\text{S}$ contacts in the range 2.40-2.71 Å and corresponding $\nu(\text{S-S})$ 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% $\nu(\text{S-S})$ 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 $\nu(\text{S-S})$ 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 $(\text{C})\text{S}\cdots\text{S}(\text{C})$ 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 $(\text{C})\text{S}\cdots\text{S}(\text{C})$ 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, $\{\text{Cu}_2[(\text{SH}_2\text{P})_2\text{CSSC}(\text{PH}_2\text{S})_2]\}$ (**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 $\text{Cu}\cdots\text{S}(\text{C})$ and $(\text{C})\text{S}\cdots\text{S}(\text{C})$ 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 $(\text{C})\text{S}\cdots\text{S}(\text{C})$ bond to 2.335 Å, two markedly different $\text{Cu}\cdots\text{S}(\text{C})$ interactions of 2.376 and 3.061 Å, and an overall C_i 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_i 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 $(\text{C})\text{S}\cdots\text{S}(\text{C})$ bonding interaction originates from the overlap of the formally singly occupied MOs of the anionic radicals $[(\text{S})\text{C}(\text{PH}_2\text{S})_2]^{-}$, 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_i 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 $(\text{C})\text{S}\cdots\text{S}(\text{C})$ anti-bonding

orbital for the isomer with a C_i 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_i 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 \cdots 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5c** in which a singlet is observed (no $^2J(^{31}\text{P},^{31}\text{P})$ 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,^[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_2M_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.^[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 $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^-$. 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.^[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 PBE/PBE 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.^[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 perturbational 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 S₂Cu₂ 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 S₂Cu₂ 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 PBE/PBE 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 S₂Cu₂ 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 d¹⁰-d¹⁰ 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 Li₂**4b** and Li₂**4c** 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 ³¹P{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 ²J(³¹P,³¹P) = 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]}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, $[(E)C(PPh_2S)_2]^{2-}$ (**3b**, E = Se; **3c**, E = S) rather than the corresponding radical anions, $[(E)C(PPh_2S)_2]^{\bullet-}$, as was also inferred from the ^{31}P NMR data.^[35] 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 d^{10} - d^8 close contacts have been reported,^[32a, 36-39] and theoretical studies on the nature of these interactions have been performed.^[37b, 37c, 38] Typically these compounds are constructed by interaction of Au(I) and Au(III) sources^[37] or by the (sometimes spontaneous) reduction of a Au(III)/Au(III) precursor.^[35, 39] 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,^[36a] a number of reports indicate the spontaneous isomerization of Au(II)/Au(II) precursors into mixed oxidation state Au(I)/Au(III) complexes.^[36] 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**.^[8] 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.^[37, 38] 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.^[26, 32] 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.^[36, 39] 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. $\angle\text{S-Au(I)-S} = 169.9(3)^\circ$ in $[\text{Au}_2\{\text{PhP}(\text{C}_6\text{H}_4\text{S})_2\}_2]$ 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 $\Sigma \angle\text{C} = 341\text{--}345^\circ$, which are, however, consistent with the values observed in the group 12, 14 and 16 complexes of the dianion **3a**, $\{\text{M}_n[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]_2\}$ ($n = 1, \text{M} = \text{Sn, Te}; n = 2, \text{M} = \text{Hg}$).^[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°, 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_2Cl_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⁻¹cm⁻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 ³¹P{¹H} 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 $d \rightarrow d$ transitions of the Au(I) and Au(III) centers, however their relatively high extinction coefficient values (~ 1500 and $2300 \text{ M}^{-1}\text{cm}^{-1}$ 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, $\{\text{Cu}_2[(\text{E}'\text{Ph}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{E}')_2]\}$ (**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 $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^{*-}$, 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 \rightarrow 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_4N_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 $\text{Ag}\cdots\text{Se}(\text{C})$ 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 $\text{Ag}\cdots\text{Se}(\text{C})$ 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 $\text{Ag}\cdots\text{S}(\text{C})$ 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 ^7Li (absence of LiCl by-product).

Spectroscopic methods

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained in CD_2Cl_2 at 23 °C on a Bruker DRX 400 spectrometer operating at 399.46 and 161.71 MHz, respectively. ^1H NMR spectra are referenced to the solvent signal and the chemical shifts are reported relative to $(\text{CH}_3)_4\text{Si}$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are referenced externally and the chemical shifts are reported relative to an 85% solution of H_3PO_4 .

X-ray crystallography

Crystallographic data for **5c**, **6b**, **7b** and **7c** are summarized in Table 1. Crystals 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**· $(\text{CH}_2\text{Cl}_2)_2$], $\{\text{Ag}_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2]\}$ (**6b**), $\{\text{Au}[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2\}$ [**7b**· $(\text{CH}_2\text{Cl}_2)_2$] and $\{\text{Au}[(\text{S})\text{C}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2\}$ [**7c**· $(\text{CH}_2\text{Cl}_2)_2$] were coated with Paratone 8277 oil and mounted on a glass fibre. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 -CH₂ hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for -CH and -CH₂ 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)₂CSeSeC(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 × 10³ M⁻¹cm⁻¹).

Spectroscopic data of {Cu₂[(SPh₂P)₂CSeSeC(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 × 10³ 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

CuCl₂ (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 {Cu₂[(SPh₂P)₂CSSC(PPh₂S)₂]} (**5c**) as a dark blue powder (0.192 g, 59%). Elemental analysis calcd (%) for C₅₀H₄₀Cu₂P₄S₆: C, 55.46; H, 3.73; found: C, 55.43; H, 3.94. ¹H NMR (CD₂Cl₂, 23 °C): δ 7.05-7.58 [m, 40H, C₆H₅]; ³¹P{¹H}: δ 59.6. UV-Vis (CH₂Cl₂): 423 nm (ε = 3.6 × 10³ M⁻¹cm⁻¹) and 634 nm (ε = 5.0 × 10³ M⁻¹cm⁻¹). ¹³C NMR spectrum could not be recorded due to poor solubility of the compound. X-ray quality crystals were obtained from the CH₂Cl₂ solution of **5c** after 24 h at 23 °C.

Method B. A mixture of [Li(TMEDA)]₂[(SPh₂P)₂CSSC(PPh₂S)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 Et₂O (30 mL) and toluene (30 mL) affording {Cu₂[(SPh₂P)₂CSSC(PPh₂S)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/CH₂Cl₂ mixture).

Synthesis of {Ag₂[(SPh₂P)₂CSeSeC(PPh₂S)₂]} (6b**).** A mixture of [Li(TMEDA)]₂[(SPh₂P)₂CSeSeC(PPh₂S)₂] (0.259 g, 0.20 mmol) and AgOSO₂CF₃ (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 {Ag₂[(SPh₂P)₂CSeSeC(PPh₂S)₂]} (**6b**) as a brownish red powder (0.235 g, 93%). Elemental analysis calcd (%) for C₅₀H₄₀Ag₂P₄S₄Se₂: C, 47.40; H, 3.18; found: C, 47.32; H, 3.25. ¹H NMR (CD₂Cl₂, 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 ($\epsilon = 6.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). 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 ($\epsilon = 8.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). 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 ($\epsilon = 6.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), 523 nm ($\epsilon = 4.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) and 651 nm ($\epsilon = 1.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). 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 °C.

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 °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 Et₂O (50 mL) affording {Au[(S)C(PPh₂S)₂]}₂ (**7c**) as a dark red powder (0.122 g, 90%). ¹H NMR (CD₂Cl₂, 23 °C): 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 °C.

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Table 1. Crystallographic data for $\{\text{Cu}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]\cdot(\text{CH}_2\text{Cl}_2)_2\}$ [**5c**·(CH_2Cl_2)₂], $\{\text{Ag}_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2]\}$ (**6b**), $\{\text{Au}[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]\cdot(\text{CH}_2\text{Cl}_2)_2\}$ [**7b**·(CH_2Cl_2)₂] and $\{\text{Au}[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]\cdot(\text{CH}_2\text{Cl}_2)_2\}$ [**7c**·(CH_2Cl_2)₂].^a

	5c	6b	7b	7c
emp. formula	$\text{C}_{52}\text{H}_{44}\text{Cl}_4\text{Cu}_2\text{P}_4\text{S}_6$	$\text{C}_{50}\text{H}_{40}\text{Ag}_2\text{P}_4\text{S}_4\text{Se}_2$	$\text{C}_{52}\text{H}_{44}\text{Au}_2\text{Cl}_4\text{P}_4\text{S}_4\text{Se}_2$	$\text{C}_{52}\text{H}_{44}\text{Au}_2\text{Cl}_4\text{P}_4\text{S}_6$
Fw	1253.99	1266.60	1614.65	1520.84
cryst. system	Triclinic	Monoclinic	Triclinic	Triclinic
space group	P-1	$\text{P}2_1/\text{n}$	P-1	P-1
<i>a</i> , Å	10.500(2)	10.534(2)	11.141(2)	11.129(2)
<i>b</i> , Å	10.960(2)	18.142(4)	15.748(3)	15.715(3)
<i>c</i> , 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)
<i>V</i> , Å ³	2669.3(9)	2382(1)	2769(1)	2750(1)
<i>Z</i>	2	2	2	2
<i>T</i> , °C	-100	-100	-100	-100
ρ_{calcd} , g/cm ³	1.560	1.766	1.937	1.836
$\mu(\text{Mo K}\alpha)$, mm ⁻¹	1.388	2.696	7.103	5.902
crystal size, mm ³	0.12×0.10×0.06	0.08×0.06×0.02	0.10×0.08×0.02	0.10×0.08×0.02
<i>F</i> (000)	1276	1252	1548	1476
Θ range, deg	2.08-25.03	2.19-25.03	2.79-25.03	2.80-25.03

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 [$I > 2\sigma(I)$] ^b	0.0740	0.0564	0.0635	0.0525
wR_2 (all data) ^c	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 λ (MoK α) = 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 {Cu₂[(SPh₂P)₂CSSC(PPh₂S)₂]}·(CH₂Cl₂)₂ [5c·(CH₂Cl₂)₂] and {Ag₂[(SPh₂P)₂CSeSeC(PPh₂S)₂]} (6b).

5c (molecule A)					
S5...S5 ^a	2.540(4)	Cu1-S5	2.535(2)	C1-P1	1.759(6)
Cu1-S1	2.230(2)	Cu1-S5 ^a	2.361(2)	C1-P2	1.775(7)
Cu1-S2 ^a	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-S5 ^a	126.71(7)	Cu1-S1-P1	97.20(9)	P1-C1-P2	127.0(3)
S1-Cu1-S2 ^a	127.96(8)	Cu1 ^a -S2-P2	98.28(9)	C1-P1-S1	114.1(2)
Cu1-S5-Cu1 ^a	117.62(8)	P1-C1-S5	112.5(4)	C1-P2-S2	111.5(2)
5c (molecule B)					
S6...S6 ^b	2.720(3)	Cu2-S6	2.284(2)	C2-P3	1.782(7)
Cu2-S3	2.257(2)	Cu2-S6 ^b	2.529(2)	C2-P4	1.769(6)
Cu2-S4 ^b	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-S6 ^b	127.58(7)	Cu2-S3-P3	99.56(9)	P3-C2-P4	128.8(4)
S3-Cu2-S4 ^b	127.63(8)	Cu2 ^b -S4-P4	95.42(9)	C2-P3-S3	111.1(2)
Cu2-S6-Cu2 ^b	111.39(8)	P3-C2-S6	120.2(4)	C2-P4-S4	113.5(2)
6b					
Se1-Se1 ^c	2.510(2)	Ag1-Se1	2.856(1)	C1-P1	1.755(7)
Ag1-S1	2.420(2)	Ag1-Se1 ^c	3.200(1)	C1-P2	1.739(7)
Ag1-S2 ^c	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-Se1 ^c	109.9(2)	Ag1-S1-P1	98.08(9)	P1-C1-P2	132.8(4)
S1-Ag1-S2 ^c	161.46(7)	Ag1 ^c -S2-P2	100.37(9)	C1-P1-S1	113.8(3)
Ag1-Se1-Ag1 ^c	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 {Au[(Se)C(PPh₂S)₂](CH₂Cl₂)₂} [7b·(CH₂Cl₂)₂] and {Au[(S)C(PPh₂S)₂](CH₂Cl₂)₂} [7c·(CH₂Cl₂)₂].^a

	7b	7c		7b	7c
Au1...Au2	3.125(1)	3.119(1)	C2-S6	1.907(14) ^a	1.754(9)
Au1-S1	2.419(3)	2.396(3)	C1-P1	1.751(14)	1.730(9)
Au1-S3	2.395(3)	2.420(2)	C1-P2	1.741(13)	1.746(9)
Au1-S5	2.441(2) ^a	2.346(2)	C2-P3	1.733(14)	1.732(9)
Au1-S6	2.451(2) ^a	2.335(3)	C2-P4	1.731(13)	1.753(9)
Au2-S2	2.289(3)	2.289(3)	P1-S1	2.039(5)	2.047(4)
Au2-S4	2.295(3)	2.294(3)	P2-S2	2.035(5)	2.029(3)
C1-S5	1.917(13) ^a	1.741(9)	P3-S3	2.057(5)	2.048(3)
			P4-S4	2.034(4)	2.039(4)
S1-Au1-S3	88.4(1)	86.86(8)	Au1-S3-P3	97.6(2)	97.3(1)
S1-Au1-S5	93.24(9) ^a	94.18(8)	Au1-S5-C1	101.3(4) ^a	104.1(3)
S1-Au1-S6	175.64(8) ^a	172.72(9)	Au1-S6-C2	101.3(4) ^a	104.3(3)
S3-Au1-S5	172.63(9) ^a	178.59(8)	Au2-S2-P2	110.5(2)	106.5(1)
S3-Au1-S6	95.29(8) ^a	92.76(8)	Au2-S4-P4	106.4(2)	108.6(1)
S5-Au1-S6	83.43(2) ^a	86.33(8)	C1-P1-S1	115.4(5)	110.9(3)
S1-Au1-Au2	91.45(8)	92.37(7)	C1-P2-S2	120.5(5)	117.7(3)
S3-Au1-Au2	90.54(9)	91.48(7)	C2-P3-S3	113.1(5)	112.7(3)
S5-Au1-Au2	96.61(5) ^a	87.53(7)	C2-P4-S4	118.5(4)	119.0(3)
S6-Au1-Au2	86.14(4) ^a	94.90(7)	P1-C1-S5	104.9(7) ^a	109.0(5)
S2-Au2-S4	155.3(1)	156.69(9)	P2-C1-S5	114.6(7) ^a	115.5(5)
S2-Au2-Au1	100.86(9)	99.48(7)	P3-C2-S6	107.2(7) ^a	107.4(5)
S4-Au2-Au1	100.87(9)	101.57(7)	P4-C2-S6	114.0(8) ^a	115.2(5)
Au1-S1-P1	98.9(2)	96.6(1)	P1-C1-P2	121.4(7)	120.2(5)
			P3-C2-P4	120.8(8)	122.4(5)

^a S5 = Se1, S6 = Se2.

Table 4. Calculated (TD-PBE1PBE/def-TZVP) transition maxima for **5a-c** and **6b,c** in the visible region.

complex	$\lambda_{\max}(\text{nm})$	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**·(CH₂Cl₂)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**·(CH₂Cl₂)₂] and (b) $\{\text{Au}[(\text{S})\text{C}(\text{PPh}_2\text{S})_2] \cdot (\text{CH}_2\text{Cl}_2)_2\}$ [**7c**·(CH₂Cl₂)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** (Cu₂Se₆), **5b** (Cu₂S₄Se₂), **5c** (Cu₂S₆), **6b** (Ag₂S₄Se₂) and **6c** (Ag₂S₆), and (b) **7b** (Au₂S₄Se₂) and **7c** (Au₂S₆) measured in CH₂Cl₂.

Scheme 1. Syntheses of the complexes **5c**, **6b,c** and **7b,c**.

Scheme 2. Possible isomerization of compound **6b** in solution.