406 *Inorg. Chem.* **2011**, *50*, 406–408
DOI: 10.1021/ic101866v

Inorganic Chemistry
Communication

Identification of a Novel η^2-Se_2 Bonding Mode in Cu(I) Complexes of the Dimeric Selenocarbonyl Dianions, $[(EPh_2P)_2CSeSeC(PPh_2E)_2]^{2-}$ (E = S, Se)

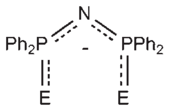
Maarit Risto, Jari Konu, and Tristram Chivers*

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, AB T2N 1N4, Canada

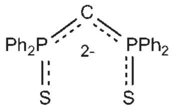
Received September 10, 2010

A metathetical reaction between $[Li(TMEDA)][(H)C(PPh_2Se)_2]$ and $CuCl_2$ in a 2:1 molar ratio afforded the dimeric Cu(I) complex, $\{Cu_2\text{-}\eta^2{:}\eta^2\text{-}[(EPh_2P)_2CSeSeC(PPh_2E)_2]\}$ (E = Se), via a selenium−proton exchange *and* an internal redox process. The analogous sulfur-containing complex (E = S) was obtained by the reactions of the dianions $[(Se)C(PPh_2S)_2]^{2-}$ and $[(SPh_2P)_2CSeSeC(PPh_2S)_2]^{2-}$ with Cu(II) and Cu(I) halides, respectively. Structural characterization of the Cu(I) complexes reveals a unique η^2-Se_2 bonding mode for the generic diselenide ligand system RSe−SeR.

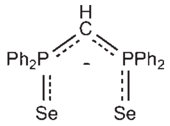
In contrast to the extensively studied *N*-bridged, monoanionic ligands $[N(PPh_2E)_2]^-$ (**1**, E = S, Se), which predominantly form *E*,*E*′-chelated metal complexes without the participation of the N atom,[1,2] the isoelectronic *C*-bridged dianion $[C(PPh_2S)_2]^{2-}$ (**2**)[3] exhibits strong metal−carbon interactions in a variety of complexes with main group[4] and transition metals,[3,5] as well as with lanthanides[6] and actinides.[7] Unusual carbon-centered reactivity is also observed in the coordination chemistry of the related diseleno *C*-bridged monoanion $[(H)C(PPh_2Se)_2]^-$ (**3**) (isoelectronic with the dithio dianion **2**). Although the expected homoleptic group 12 complexes are formed via metathesis of $[Li(TMEDA)]$**3** with $M(II)Cl_2$ (M = Zn, Hg),[8] an unprecedented *Se−H⁺ exchange* occurs in reactions with group 14 and 16 element dihalides (M = Sn, Te) to give homoleptic M(IV) complexes of the triseleno dianion $[(Se)C(PPh_2Se)_2]^{2-}$ (**4a**).[9] Furthermore, a binuclear Hg(II) complex of the dianion **4a** is obtained from mild thermolysis of the homoleptic Hg(II) compound of the monoanion **3**,[9] and monomeric Pb(II) complexes of the related trichalcogeno dianions **4b** and **4c** are formed by chalcogen insertion into the Pb−C bond of dimeric Pb(II) complexes of **2**.[4a]



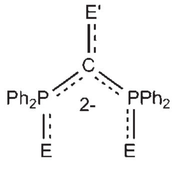
1



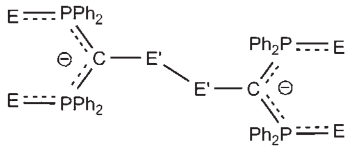
2



3



4a (E = E' = Se)
4b (E = E' = S)
4c (E= S; E' = Se)



5a (E = E' = Se)
5b (E = E' = S)
5c (E = S, E' = Se)

In light of these structurally diverse complexes of the dianions **4**, we recently developed an efficient synthetic route to dilithium derivates of the ligands **4b** and **4c** for utilization in both redox and coordination chemistry.[10] In preliminary studies, the one-electron oxidation of **4b** and **4c** produced the novel dichalcogenides $[(EPh_2P)_2CE'E'C(PPh_2E)_2]^{2-}$ (**5b**, E = E′ = S; **5c**, E = S, E′ = Se) that are formally dimers of the corresponding radical anions $[(E')C(PPh_2E)_2]^{\bullet-}$ with elongated central chalcogen−chalcogen bonds.[10] The coordination

---

*To whom correspondence should be addressed. E-mail: chivers@ucalgary.ca.

[1] For reviews, see: (a) Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.* **2001**, *223*, 117. (b) Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 2893. (c) Haiduc, I. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Ltd.: Amsterdam, 2003; pp 323−347.

[2] Some exceptions that involve *N*-coordination have been reported, primarily for lanthanides: (a) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1216, 1222. Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1999**, *38*, 5478. Also for Pd: (b) Necas, M.; Foreman, M. R. St. J.; Marek, J.; Woollins, J. D.; Novosad, J. *New J. Chem.* **2001**, *25*, 1256.

[3] (a) Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 6382. (b) Cantat, T.; Ricard, L.; Jean, Y.; Le Floch, P.; Mézailles, N. *Organometallics* **2006**, *25*, 4965.

[4] (a) Leung, W.-P.; Wa, C.-L.; Kan, K.-W.; Mak, T. C. W. *Organometallics* **2010**, *29*, 814. (b) Foo, C.; Lau, K.-C.; Yang, Y-F; So, C.-W. *Chem. Commun.* **2009**, 6816.

[5] (a) Cantat, T.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 6030. (b) Cantat, T.; Demange, M.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Organometallics* **2005**, *24*, 4838.

[6] (a) Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mézailles, N. *Organometallics* **2006**, *25*, 1329. (b) Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem. Commun.* **2005**, 5178.

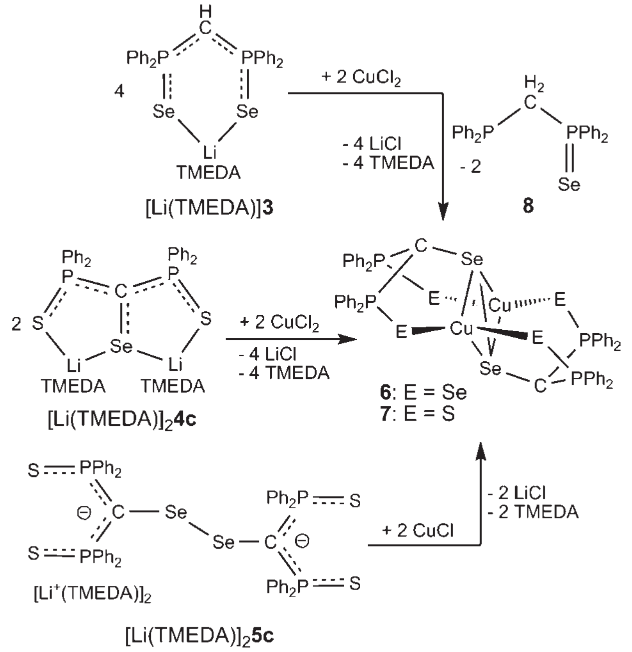
[7] (a) Tourneux, J.-C.; Berthet, J-C; Thuéry, P.; Mézailles, N.; Le Floch, P.; Ephritikhine, M. *Dalton Trans.* **2010**, *39*, 2494. (b) Cantat, T.; Arliguie, T.; Noël, A.; Thuéry, P.; Ephritikhine, M.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2009**, *131*, 963.

[8] Konu, J.; Tuononen, H. M.; Chivers, T. *Inorg. Chem.* **2009**, *48*, 11788.

[9] Konu, J.; Chivers, T. *Chem. Commun.* **2010**, *46*, 1431.

[10] Konu, J.; Chivers, T.; Tuononen, H. M. *Chem.*—*Eur. J.* **2010**, *16*, 12977.

Scheme 1. Syntheses of the Copper Complexes **6** and **7**



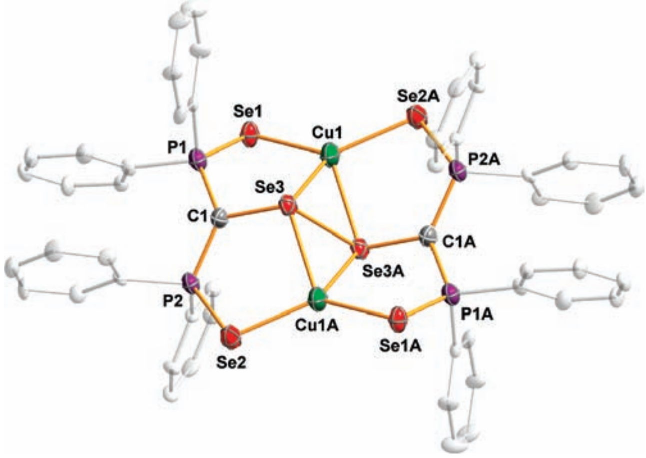


Figure 1. Molecular structure of **6**·(CH$_2$Cl$_2$)$_2$ with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvate molecules have been omitted for clarity. Relevant bond parameters (in Å and deg): Se3–Se3A 2.683(2), Cu1–Se3 2.669(2), Cu1–Se3A 2.453(1), Cu1–Se1 2.339(2), Cu1–Se2A 2.344(2), C1–Se3 1.855(7), C1–P1 1.758(7), C1–P2 1.767(7), P1–Se1 2.183(2), P2–Se2 2.163(2), P1–C1–P2 127.6(4), P1–C1–Se3 110.6(4), P2–C1–Se3 121.0(4). Symmetry operation: (A) 1 − *x*, 1 − *y*, 1 − *z*.

chemistry of these dianionic ligands is potentially multifarious and includes the possibility of an η^2-E$_2$ bonding mode, which is unknown for E = Se.[11] The more common behavior, especially if the metal center can attain a higher valence state, is oxidative addition (insertion into an E–E bond).[12] In this context, we report three different syntheses of the binuclear Cu(I)/Cu(I) complexes, {Cu$_2$-η^2:η^2-[(EPh$_2$P)$_2$CSeSeC(PPh$_2$E)$_2$]} (**6**: E = Se, **7**: E = S), which are the first examples of the η^2-Se$_2$ bonding mode for generic RSe–SeR ligands. In addition, the preparation of **7** represents the first use of the novel ligands **4c** and **5c** for the construction of transition-metal complexes.

Complex **6** was obtained by the aforementioned Se–H$^+$ exchange process[9] from the reaction between [Li(TMEDA)]**3** and CuCl$_2$ in a 2:1 molar ratio. Monitoring this reaction by ^{31}P NMR spectroscopy revealed the continuous depletion of the monoanion **3** and the formation of the monoselenide [(H$_2$)C(PPh$_2$)(PPh$_2$Se)][13] (**8**) (Scheme 1). The complete consumption of the starting material was achieved by heating the reaction mixture at 60 °C for 18 h. The resulting gray powder displayed a singlet at 49.8 ppm with ^{77}Se satellites [$^1J(^{31}$P,^{77}Se) = 561 Hz and $^2J(^{31}$P,^{31}P) = 51.1 Hz] in the ^{31}P{^{1}H} NMR spectrum measured in CD$_2$Cl$_2$. The ^{1}H NMR spectrum of the product showed only the typical signal pattern for phenyl groups, and no signal for the PC(H)P hydrogen was observed.

Recrystallization of the product from hexane-CH$_2$Cl$_2$ produced dark brown plate-shaped crystals. The single crystal X-ray structure determination revealed a dimer, {Cu$_2$-η^2:η^2-[(SePh$_2$P)$_2$CSeSeC(PPh$_2$Se)$_2$]}·(CH$_2$Cl$_2$)$_2$ [**6**·(CH$_2$Cl$_2$)$_2$], in which two distorted tetrahedral copper centers are coordinated to a Se atom from each terminus of the ligand and η^2-bonded to the Se–Se linkage [*d*(Se–Se) = 2.683(2) Å] (Figure 1). By contrast, the previously reported binuclear Hg(II)/Hg(II) complex, {Hg$_2$-[(Se)C(PPh$_2$Se)$_2$]$_2$}, incorporates two dianionic ligands **4a** with a nonbonding Se···Se separation of 4.609(1) Å.[9] The PC(Se)P unit in **6** exhibits a significant shortening of the C–Se bond (by ca. 0.08 Å) and an elongation of ca. 0.04 Å in the C–P bonds compared to the analogous contacts in the dianion [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ in the complexes {M$_n$[(Se)C(PPh$_2$Se)$_2$]$_2$} (*n* = 1, M = Sn, Te; *n* = 2, M = Hg).[9] The similarity of the metrical parameters in **6** with those found for the dilithium salt of the dimeric dianion **5c** (ca. 2.51, 1.89, and 1.76 Å for the corresponding Se–Se, C–Se, and C–P bonds, respectively)[10] suggests an internal redox process in which the [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ ligands (**4a**) formed from [(H)C(PPh$_2$Se)$_2$]$^-$ (**3**) by Se–H$^+$ exchange have been oxidized to the dimeric dianion, [(SePh$_2$P)$_2$CSeSeC(PPh$_2$Se)$_2$]$^{2-}$ (**5a**), with concomitant reduction of Cu(II) to Cu(I).[14]

In view of the intriguing redox process to afford the Cu(I) complex **6**, as well as the significantly elongated Se–Se bond compared to [Li(TMEDA)]$_2$**5c**,[10] we investigated the direct synthesis of an analogous binuclear copper(I) complex by using the dilithium salts of the dianions **4c** and **5c**.[10] The metathetical reactions of these reagents with Cu(II) and Cu(I) halides, respectively, circumvent the mechanistically obscure Se–H$^+$ exchange process (Scheme 1).

The reactions of (a) [Li(TMEDA)]$_2$**4c** with CuCl$_2$ in 1:1 molar ratio and (b) [Li(TMEDA)]$_2$**5c** and CuCl in 1:2 molar

---

[11] The CCDC database revealed no structurally characterized complexes with the η^2-E$_2$ bonding mode for REER ligands when E = Se, and only Nb and Ti examples can be found for E = S: (a) McKarns, P. J.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 4743. (b) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321.

[12] For recent examples, E = S: (a) Siemeling, U.; Bretthauer, F.; Bruhn, C. *J. Organomet. Chem.* **2010**, *695*, 626. (b) Figueroa, J. S.; Yurkerwich, K.; Melnick, J.; Buccella, D.; Parkin, G. *Inorg. Chem.* **2007**, *46*, 9234. E = Se:(c) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *J. Organomet. Chem.* **2001**, *623*, 168.

[13] Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

[14] A related selenium-proton exchange has been observed in the formation of a trinuclear Cu(I)/Cu(I)/Cu(II) complex containing the neutral ligand SeC(Ph$_2$PO)$_2$ which was isolated in an unspecified yield from the reaction of H$_2$C(PPh$_2$Se)$_2$ and the hydrated salt CuCl$_2$·2H$_2$O. Cauzzi, D.; Graiff, C.; Lanfranchi, M.; Predieri, G.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2443.

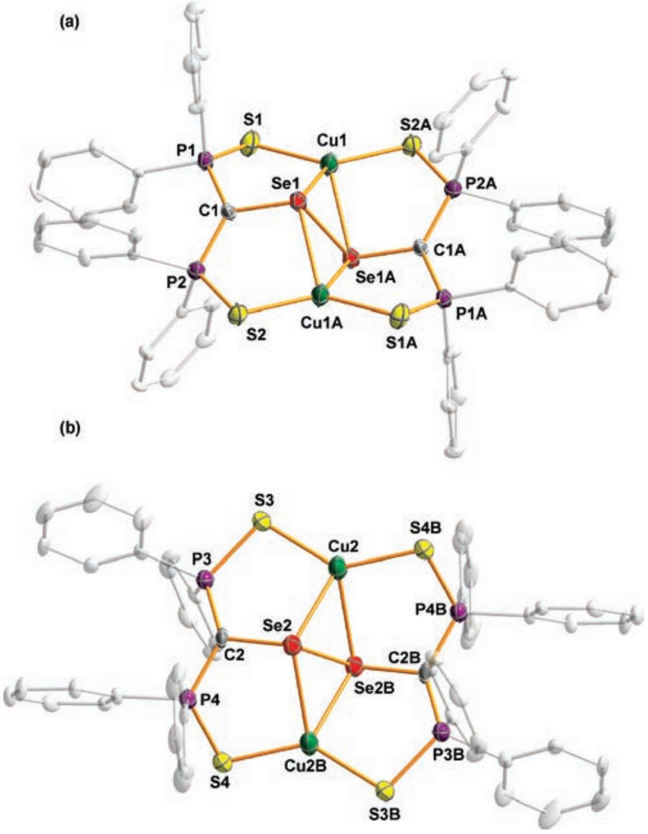


Figure 2. Two independent molecules in the crystal structure of $7\cdot(CH_2Cl_2)_2$ with atomic numbering scheme. Hydrogen atoms and solvate molecules have been omitted for clarity. Relevant bond parameters (in Å and deg) in molecule A: Se1−Se1A 2.610(2), Cu1−Se1 2.627(2), Cu1−Se1A 2.537(2), Cu1−S1 2.227(2), Cu1−S2A 2.220(2), C1−Se1 1.853(7), C1−P1 1.745(7), C1−P2 1.763(7), P1−S1 2.015(3), P2−S2 2.010(3), P1−C1−P2 128.1(4), P1−C1−Se1 111.8(4), P2−C1−Se1 119.8(4); and in molecule B: Se2−Se2B 2.688(2), Cu2−Se2 2.455(2), Cu2−Se2B 2.691(2), Cu2−S3 2.227(3), Cu2−S4B 2.219(2), C2−Se2 1.871(7), C2−P3 1.752(9), C2−P4 1.739(8), P3−S3 2.007(3), P4−S4 2.030(3), P3−C2−P4 130.6(4), P3−C2−Se2 119.1(4), P4−C2−Se2 109.2(4). Symmetry operations: (A) $2 - x, 1 - y, -z$ and (B) $1 - x, 1 - y, 1 - z$.

ratio at −80 °C proceeded cleanly to afford a dark red powder in 62 and 85% yields, respectively (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the product from both reactions displayed a singlet at 59.5 ppm suggesting the formation of the same product *in both reactions*. Single crystals suitable for an X-ray structural determination were obtained by recrystallization of this product from a pentane-CH_2Cl_2 mixture.

The crystal structure of the CH_2Cl_2 solvate, $\{Cu_2\text{-}\eta^2{:}\eta^2\text{-}[(SPh_2P)_2CSeSeC(PPh_2S)_2]\}\cdot(CH_2Cl_2)_2$ [$7\cdot(CH_2Cl_2)_2$], revealed the isostructural relationship of the Cu(I) complex **7** with the all-selenium derivative **6**. The structure of $7\cdot(CH_2Cl_2)_2$ displays two independent molecules in the crystal lattice (Figure 2). While both discrete molecules of **7** (A and B) exhibit a geometrical arrangement comparable to that in **6**, the metrical parameters in the central Cu_2Se_2 unit show a notable disparity. Intriguingly, the (C)Se−Se(C) bond length of 2.688(2) Å in molecule B is ca. 0.08 Å longer than that of 2.610(2) Å in molecule A, and the Cu−Se bonds in molecule B also show a rather wide range of 2.455(2)−2.691(2) Å while those in molecule A span a narrower range of 2.537(2)−2.627(2) Å. Inspection of the Se−Se and Cu−Se bond lengths in complexes **6** and **7** discloses a correlation in which an elongation of the shortest Cu−Se(C) distance results in a stronger Se−Se contact; cf. Cu−Se/Se−Se distances of 2.453(1)/2.683(2) Å in **6** and 2.455(2)/2.688(2) Å in molecule B in **7** vs 2.537(2)/2.610(2) Å in molecule A in **7**.

In summary, binuclear Cu(I)/Cu(I) complexes of the dianionic ligands $[(EPh_2P)_2CSeSeC(PPh_2E)_2]^{2-}$ (E = S, Se) have been prepared in three different ways. They display a novel η^2-Se_2 bonding mode for RSe−SeR ligands. The elongation and flexibility of the (C)Se−Se(C) bonds in **6** and **7** suggest the likelihood of oxidative insertion for other electron-rich transition metal centers accompanied by the intriguing possibility of isolating metal complexes of the monoanion radicals $[(E)C(PPh_2S)_2]^{\bullet -}$. In addition, the redox chemistry of the all-sulfur system **5b** merits investigation in view of the biological significance of copper−disulfide interactions.[15]

Acknowledgment. The authors gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council (Canada).

Supporting Information Available: Experimental and crystallographic data in pdf format, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[15] Srogl, J.; Hývl, J.; Révész, A.; Schröder, D. *Chem. Commun.* **2009**, 3463.