

Copper-promoted Intramolecular Selenium Transfer from a P=Se Group to a P-CH₂-P Methylene Carbon producing an Unusual Methaneselone Ligand

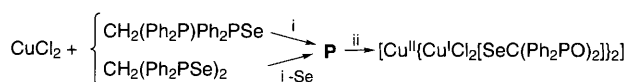
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The bis(diphenylphosphino)methane selenides CH₂(Ph₂P)Ph₂PSe and CH₂(Ph₂PSe)₂, react with copper(II) chloride giving an unidentified copper(I) complex; exposure to the air affords the new bifunctional, tridentate ligand bis(diphenylphosphoryl)methaneselone SeC(Ph₂PO)₂ linking copper(I) and copper(II) in the trinuclear complex [Cu^{II}{Cu^ICl₂[μ-SeC(Ph₂PO)₂]}₂].

The chemical properties of the diphosphine mono- or dichalcogenides of formula X(Ph₂P)Ph₂PE and X(Ph₂PSe)₂ (X = CH₂, NH and E = S, Se) have attracted continuous interest over the last two decades, particularly because they behave as soft-donor chelating ligands, several complexes with divalent metal cations or metal carbonyl fragments having been characterized with these ligands in the neutral or anionic form.¹

The second interesting property of these molecules is the frailty of the P=E bond, which leads to two classes of useful processes: (i) the exchange of chalcogen between tertiary phosphines² and (ii) the synthesis of phosphine-substituted chalcogenide clusters through oxidative transfer of chalcogen atoms to zero-valent metal complexes.³ Moreover, strongly related with this general reactivity is the chalcogen extrusion *via* coordination, observed in the case of selenium, for the complex [Pt{SePPh₂CH₂}₂]²⁺ (containing two six-membered chelate rings), which turns into [Pt{SePPh₂(PPh₂)CH₂}₂]²⁺ with a favourable steric configuration, *i.e.* two five-membered chelate rings.⁴



Scheme 1 Reagents and conditions: i, EtOH-MePh, N₂, room temp., ii, recrystallisation from CH₂Cl₂-hexane, air

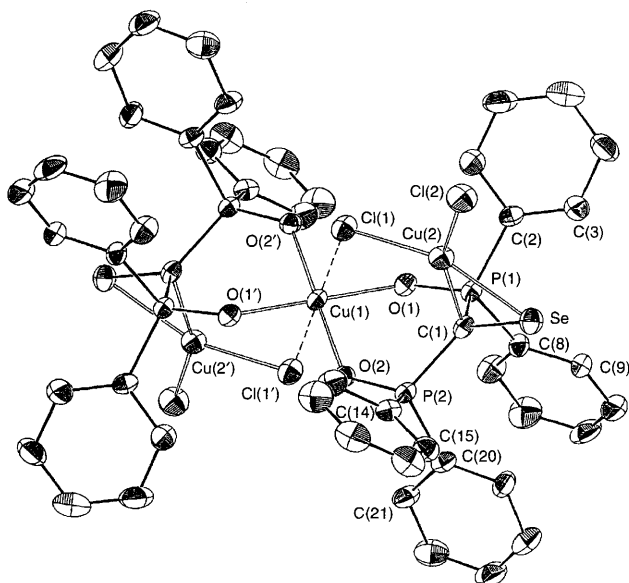


Fig. 1 View of the molecular structure of the molecule [Cu{CuCl₂[μ-SeC(Ph₂PO)₂]}₂] **1** together with the atomic numbering system. Selected bond distances (Å) and angles (°): Cu(1)-O(1) 1.955(5), Cu(1)-O(2) 1.952(6), Cu(1)-Cl(1) 2.802(2), Cu(2)-Cl(1) 2.199(3), Cu(2)-Cl(2) 2.176(3), Cu(2)-C(1) 2.029(8), Cu(2)-Se 2.293(2), Se-C(1) 1.846(9), O(1)-P(1) 1.501(7), O(2)-P(2) 1.499(7); O(1)-Cu(1)-O(2) 92.1(2), O(1)-Cu(1)-Cl(1) 90.2(2), O(2)-Cu(1)-Cl(1) 88.5(2), Cl(1)-Cu(2)-Cl(2) 105.0(1), Cl(1)-Cu(2)-C(1) 101.7(2), Cl(2)-Cu(2)-Se 103.1(1), C(1)-Cu(2)-Se 50.1(2), Cu(1)-O(1)-P(1) 133.0(3), Cu(1)-O(2)-P(2) 132.2(4).

We report here on the unprecedented reactions[†] between copper(II) chloride and the bis(diphenylphosphino)methane selenides CH₂(Ph₂P)Ph₂PSe (dppmSe) and CH₂(Ph₂PSe)₂ (dppmSe₂), which produce the trinuclear complex [Cu^{II}{Cu^ICl₂[μ-SeC(Ph₂PO)₂]}₂] **1**, under the conditions summarized in Scheme 1.

Complex **1** contains the tridentate ligand bis(diphenylphosphoryl)methaneselone SeC(Ph₂PO)₂, formed by intramolecular selenium transfer from the P=Se group to the methylene carbon, promoted by copper. The ligand, which combines the rare selone function with two phosphoryl donor fragments, forms a mixed copper(II) dicopper(I) trinuclear complex, in which the bifunctional ligand bridges two copper atoms in different oxidation states. Mechanistic details of this reaction, which does not occur with NiCl₂ or CoCl₂, have not yet been clarified; efforts are being made to characterize the rough product **P**, which should contain, as major species, a copper(I) complex of dppmSe, as suggested by the selenium extrusion when dppmSe₂ is used as reactant.

The molecular structure of the complex **1**, shown in Fig. 1, has been fully elucidated by X-ray analysis of its dichloromethane solvate.[‡] The complex has an imposed crystallographic *C*₂ symmetry. The copper(II) atom lies on the inversion centre and exhibits a tetragonally distorted octahedral environment with four oxygen atoms [bond distances of 1.955(5) and 1.952(6) Å] from the phosphoryl groups in the equatorial positions and two chlorine atoms from the dichlorocuprate(1-) groups occupying the apical positions and forming two elongated bonds of 2.802(2) Å. The six-membered chelation ring Cu(OP)₂C adopts a boat conformation, copper and carbon being shifted from the same side of the mean plane by 0.60(1) and 0.66(1) Å respectively.

The two methaneselone groups are engaged in a π-bonding interaction with the two chlorocuprate(1-) copper(I) atoms, which exhibit trigonal coordination involving the two Cl atoms and the midpoint of the C=Se bond [Cu-Se 2.293(2), Cu-C(1) 2.029(8) Å]. The C=Se bond distance, 1.846(9) Å, is significantly longer than that observed in an uncoordinated selone compound, 1.774(6) Å,⁵ but is significantly shorter than that found in (Ph₃P)₂CSe [1.990(11) Å]⁶ involving an ylide carbon atom. § Owing to metal coordination, the environment of the carbon atom C(1) is slightly pyramidally distorted, the deviation from the plane through P(1), P(2) and Se being 0.246(8) Å.

The chlorocuprate groups coordinated to the selone moieties are sterically oriented in such a way to allow the Cl-Cu²⁺ apical interactions; the copper(I) coordination plane is practically orthogonal to the copper(II) equatorial plane, with an angle of 91.3(1)° between the corresponding least-squares planes.

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Footnotes

[†] CuCl₂·2H₂O (15 mg, 0.088 mmol), dissolved in ethanol (10 cm³), was added to a toluene solution (20 cm³) of dppmSe₂ (48 mg, 0.088 mmol) and the mixture was stirred for 1 h under nitrogen. The colour changed to pale

green and a red solid (elemental selenium) was formed, which was filtered off. The solution was reduced in volume, causing the precipitation of a pale yellow powder **P**, which was filtered, washed with hexane and dried *in vacuo*. IR (KBr): 1171s, 778s, 725s, 738, 691, 510 cm^{-1} .

The same reaction was carried out with dppmSe: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (18 mg, 0.10 mmol) and dppmSe (49 mg, 0.10 mmol) were subjected to the same treatment, obtaining the same pale yellow powder, without segregation of elemental selenium.

In both cases, the powder **P** was dissolved in dichloromethane in the presence of air; slow diffusion of hexane at *ca.* 4 °C yielded green prismatic crystals of **1** suitable for X-ray analysis. IR (KBr): 1148s, 728s, 754, 691, 595, 533 cm^{-1} .

‡ *Crystal structure determination* of $[\text{Cu}\{\text{CuCl}_2[\mu\text{-SeC}(\text{Ph}_2\text{PO})_2]\}_2] \cdot 2\text{CH}_2\text{Cl}_2$, $\text{C}_{52}\text{H}_{44}\text{Cl}_8\text{Cu}_3\text{O}_4\text{P}_4\text{Se}_2$ **1**: $M = 1488.99$, monoclinic, space group $P2_1/n$, $a = 15.992(5)$, $b = 14.909(5)$, $c = 13.532(4)$ Å, $\beta = 114.90(2)^\circ$, $U = 2926(2)$ Å³, $Z = 2$, $D_c = 1.690$ g cm^{-3} , nickel-filtered $\text{Cu-K}\alpha$ radiation, $\lambda = 1.54184$ Å, $\mu = 74.33$ cm^{-1} . The intensity data were collected on a Siemens AED diffractometer, using the θ - 2θ scan technique at room temp. 5571 Unique reflections were measured (with θ in the range 3–70°) and 3640, having $I > 2\sigma(I)$, were used in the refinement. An empirical correction for absorption was applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions ($\text{C-H} = 0.96$ Å) and refined riding on the corresponding carbon atoms, isotropically. The SHELX-76 and SHELXS-86 systems of computer programs were used.⁷ The R and R_w values were 0.0666 and 0.0823 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ $(\text{Ph}_3\text{P})_2\text{CSe}$ is the selenium adduct of the double ylide hexaphenyl-carbodiphosphorane $(\text{Ph}_3\text{P})_2\text{C}$, in which the carbanionic centre of the ylide bonds acts as a donor to the selenium atom. It is obtained by reaction of

elemental selenium with $(\text{Ph}_3\text{P})_2\text{C}$ at room temp. This reaction path suggests that a carbanionic intermediate derived from coordinated $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$ could be the reactive species, which undergoes attack by selenium mediated by copper.

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