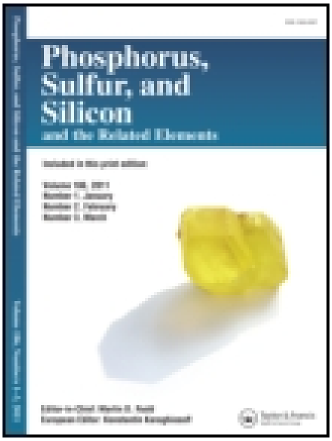

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

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To cite this article: Daniel Gallenkamp, Edward R. T. Tiekink & Fabian Mohr (2008) Gold(I) Phosphine Complexes Containing Selenocarbamate Esters: Crystal and Molecular Structure of N-phenyl-O-methylselenocarbamate, Phosphorus, Sulfur, and Silicon and the Related Elements, 183:4, 1050-1056, DOI: 10.1080/10426500801901087

To link to this article: http://dx.doi.org/10.1080/10426500801901087

Phosphorus, Sulfur, and Silicon, 183:1050–1056, 2008
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500801901087

Gold(I) Phosphine Complexes Containing Selenocarbamate Esters: Crystal and Molecular Structure of *N*-phenyl-*O*-methylselenocarbamate

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A series of both mono- and dinuclear gold(I) phosphine complexes containing deprotonated N-phenyl-O-methylselenocarbamate of the type $[AuSeC(OMe){=}NPh(P)]$ *and* $[Au_2SeC(OMe){=}NPh_2(PP)]$ *(P = PPh_3, P(o-tolyl)$_3$, PTA; PP = dppm, dppe, dppp, dppf) were prepared and characterized by spectroscopic techniques. The X-ray crystal structure of SeC(OMe)=N(H)Ph is also reported and shows the molecule to exist in the E-conformation. Centrosymmetrically related dimers associate in the crystal structure by N—H· · ·Se interactions.*

Keywords Crystal structure; N—H· · ·Se hydrogen-bonding; gold; phosphine complexes; selenium; selenocarbamate ester

INTRODUCTION

The chemistry of gold(I) phosphine complexes with sulfur ligands is today a well established field. A large number of such compounds have been prepared and some interesting applications have emerged due to their luminescent properties and biological activity.[1] Particularly in medicinal applications, gold thiolate complexes have shown much promise; the gold(I) complex auranofin (Figure 1) is one of the leading anti-arthritis drugs on the market.[2]

In contrast, the chemistry of gold(I) complexes containing selenium is relatively unexplored. The known complexes are generally restricted to those derived from selenium ligands, which are either commercially

We thank the Fonds der Chemischen Industrie as well as the University of Wuppertal for generous financial support of this work.

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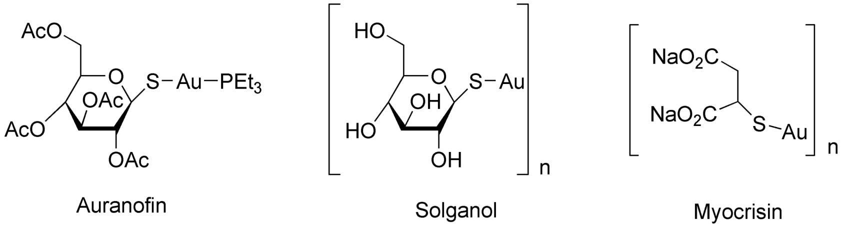
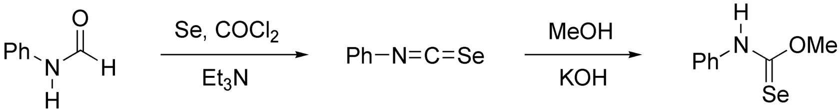


FIGURE 1 Examples for gold(I) thiolate based drugs.

available or easily accessible. The preparation, structures and photophysical properties of a series of gold(I) phosphine complexes containing *thio*carbamate esters has been reported.[3–6] In order to establish if there are differences in the behaviour of the analogous selenium analogues, we synthesized and characterized a series of gold(I) complexes containing *N*-phenyl-*O*-methylselenocarbamate. Some initial results of this investigation are communicated herein.

RESULTS AND DISCUSSION

The synthesis of *N*-phenyl-*O*-methylselenocarbamate and the cobalt(II) complexes [$CoX_2SeC(OMe)=NPh_2$] (X = Cl, Br, I) was reported as early as 1971, but since then this ligand has never been used again.[7] We obtained *N*-phenyl-*O*-methylselenocarbamate by the reaction of *N*-phenylisoselenocyanate[8] with MeOH in the presence of KOH in 80 % yield as a colorless, extremely malodorous solid (Scheme 1).



SCHEME 1

N-phenyl-*O*-methylselenocarbamate was characterized by various spectroscopic techniques including ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy, IR spectroscopy and mass spectrometry. The analogous sulfur compound exists in solution as a mixture of *E* and *Z* isomers, as was shown by low temperature[4] ^{1}H-NMR spectroscopy; in the solid-state however, the compound exists as the *E* isomer. We found that the ^{1}H-NMR spectrum of *N*-phenyl-*O*-methylselenocarbamate does not change on cooling from room temperature to −60°C, suggesting that either no conformation change occurs at all or that the conformation change is fast on the NMR timescale even at −60°C. The IR spectrum shows strong bands due to the N—H and C—N stretches at 3149 and 1537 cm^{-1}, respectively. The band due to the C=Se stretch could not be located in the

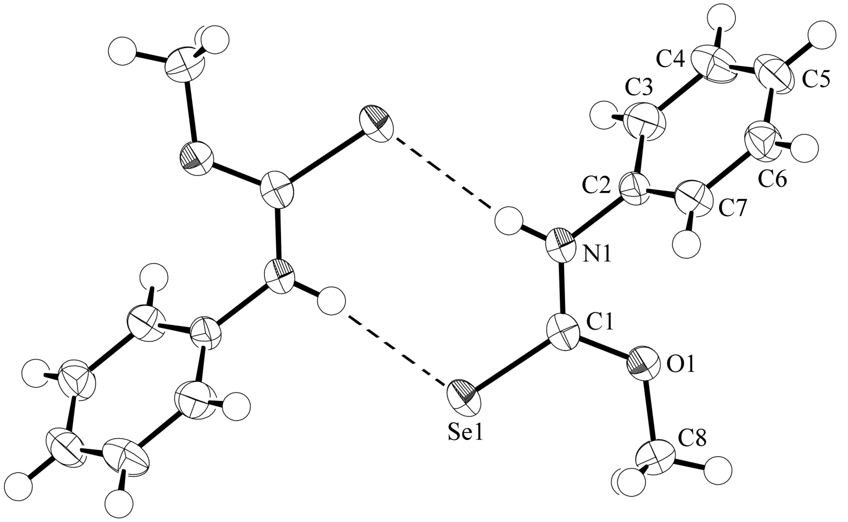


FIGURE 2 Dimer formation mediated by N–H···Se interactions in the structure of *N*-phenyl-*O*-methylselenocarbamate showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. Selected geometric parameters [Å, °]: C1–Se1 1.8322(19), C1–O1 1.322(2), C1–N1 1.328(2), Se1–C1–O1 124.60(14), Se1–C1–N1 122.07(14), O1–C1–N1 113.29(16), and C1–N1–C2 126.06(16). The dashed lines show the N–H···Se hydrogen-bonding interactions: N1–H···Se1^i = 2.60 Å, N1–H···Se1^i 3.4451(19) Å, with an angle of 162^o at H for symmetry operation *i*: -*x*, 1-*y*, 1-*z*.

fingerprint region of the spectrum. The compound was fully characterized by single-crystal X-ray diffraction methods.

The molecular structure is shown in Figure 2 and selected geometric parameters are collected in the figure caption. The central COC(=Se)N chromophore is essentially planar as seen in the Se1/C1/N1/C2 and C8/O1/C1/N1 torsion angles of 178.90(14) and 175.50(16)°, respectively. However, the N1-phenyl ring is not co-planar with these atoms: the C1/N1/C2/C3 torsion angle is 124.0(2)°. The C1=Se1 bond falls within the range expected for a C=Se double bond, *i.e.*, 1.82–1.87 Å.[9] The conformation of the molecule about the C1-N1 bond, which at 1.328(2) Å has some multiple bond character indicating restricted rotation, is *E*. The angles subtended at the C1 atom by the Se1 atom are larger than the O1–C1–N1 bond, in accord with expectation. Overall, the molecular structure is as reported for the sulfur analogue, indeed the structures are isomorphous.[4a] Molecules associate in the solid-state via N=H···Se hydrogen-bonding interactions. The dimeric units thus formed are connected into supramolecular chains aligned along the

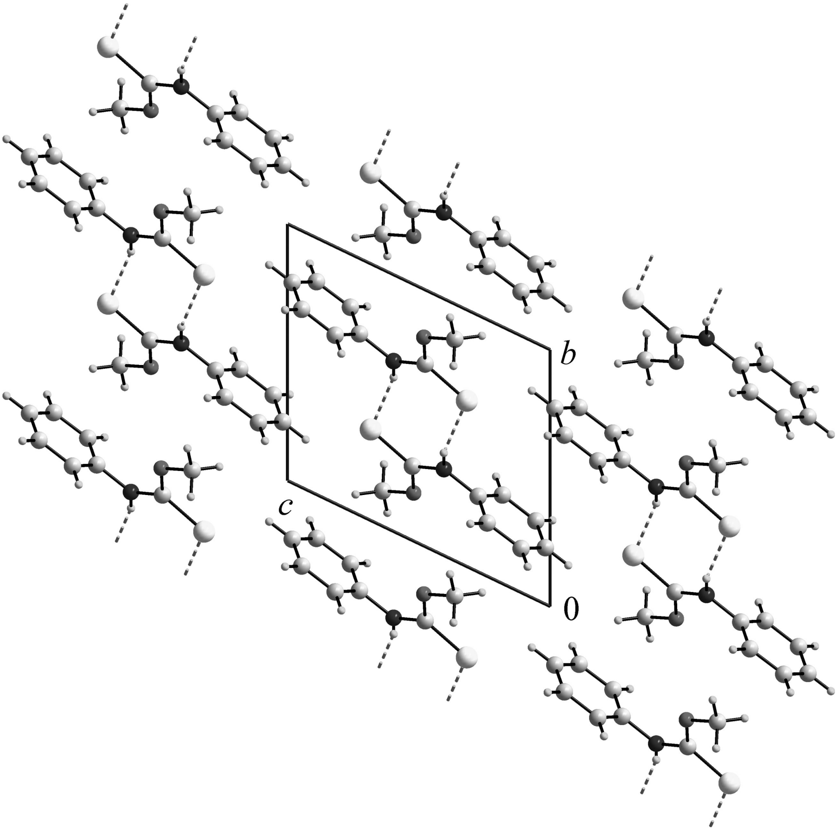
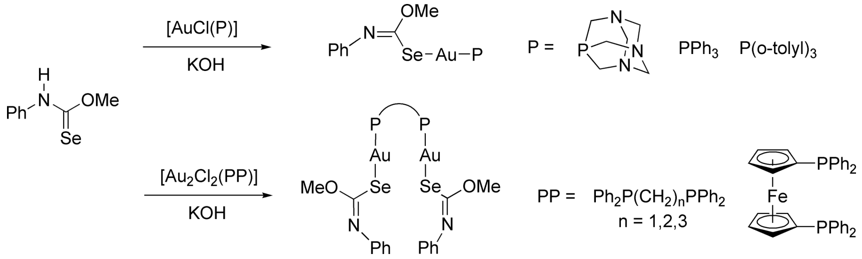


FIGURE 3 Unit cell contents for *N*-phenyl-*O*-methylselenocarbamate viewed down the *a*-direction. Dashed lines represent C–H· · ·Se hydrogen-bonding interactions.

a-direction via C=H· · ·Se interactions.[10] These chains are connected to adjacent chains via weak $\pi \cdots \pi$ interactions to form layers that stack along the *b*-direction. Connections between layers are of the type C–H· · ·π; a view of the unit cell contents down the *a*-direction, is shown in Figure 3.

A series of both mono- and dinuclear gold(I) phosphine complexes were prepared by deprotonation of *N*-phenyl-*O*-methylselenocarbamate in the presence of the appropriate chlorophosphinegold(I) complexes as shown in Scheme 2. The new gold complexes could be isolated as colorless or pale-yellow solids in good yields and were characterized by ^{1}H and ^{31}P-NMR spectroscopy and IR spectroscopy.[11] The combination of the poor solubility of the compounds



SCHEME 2

and the extremely low sensitivity of the ^{77}Se nucleus did not allow us to obtain any ^{77}Se-NMR spectra. The chemical shifts of the singlet resonances in the ^{31}P-NMR spectra are typical for phosphinegold(I) complexes. Deprotonation of the ligand is confirmed in both the ^{1}H and IR spectra through the absence of signals due to the NH group. In addition, the C—N stretching frequencies in the IR spectra are shifted to higher wave numbers (*ca.* 1620 cm^{-1}) compared to those of the protonated ligand. These complexes thus represent the very first examples of metal complexes containing deprotonated *N*-phenyl-*O*-methylselenocarbamate. The solid-state structures of the binuclear complexes containing 1,2-bis(diphenylphosphino)ethane (dppe) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were determined by single crystal X-ray diffraction. While the full crystallographic details will be published separately, the results show some very interesting and unique features. In both cases, the gold atoms are oriented away from each other, which means that no short intramolecular Au· · ·Au interactions are possible.

In conclusion, we present here the preparation and characterisation of the first gold(I) phosphine complexes containing deprotonated *N*-phenyl-*O*-methylselenocarbamate ligands. Further studies of this class of compounds as well as their luminescence properties are currently in progress.

EXPERIMENTAL

N-phenyl-*O*-methylselenocarbamate was prepared as described for the sulfur analog[4b] from *N*-phenylisoselenocyanate[8] in 80 % yield. ^{1}H-NMR (CDCl$_3$): $\delta = 4.26$ (s, 3H, OMe), 7.17-7.41 (m, 5 H, Ph), 9.02 (br. S, 1 H, NH); ^{77}Se-NMR (acetone-d_6): $\delta = 279$ (s); IR (KBr disk): $\nu = 3149$ (N-H), 1537 (N-C) cm^{-1}; LS-MS (*m*/*z*): 215 [*M*]$^+$, 430 [*M*$_2$]$^+$.

X-Ray Crystallography

Intensity data for *N*-phenyl-*O*-methylselenocarbamate, grown from the slow evaporation of a dichloromethane solution of the compound, were measured at 153 K on a Rigaku AFC12/Saturn724 CCD fitted with Mo Kα radiation. Data processing and absorption correction were accomplished with Crystal Clear[12] and ABSCOR,[13] respectively. The structure was solved by direct-methods[14] and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2)+ (0.033P)^2+ 0.249P]$ for $P = (F_o^2+ 2F_c^2)/3$) was on F^2.[15]

Crystal Data

C_8H_9NOSe, $M = 214.12$, triclinic space group P-1, $a = 5.8383(8)$ Å, $b = 8.4283(13)$ Å, $c = 9.8029(9)$ Å, $\alpha = 63.798(12)^o$, $\beta = 76.045(15)^o$, $\gamma = 84.134(18)^o$, $V = 420.02(9)$ Å^3, $Z = 2$, $D_x = 1.693$ g cm^{-3}, $\mu = 4.409$ mm^{-1}, $\theta_{\max} = 26.5^o$, 1750 independent data, 1733 data with $I \geq 2\sigma(I)$, $R = 0.024$, Rw (all data) $= 0.060$, $\rho_{\max} = 0.46$ e Å^{-3}. CCDC deposition number: 651738.

Figures 2 and 3 were drawn with the ORTEP[16] and DIAMOND[17] programmes, respectively. Data manipulation and interpretation were with teXsan[18] and PLATON.[19]

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-x, 1-y, 2-z. C–H$\cdots\pi$: C8–H8b$\cdots$ring centroid(C3-C7)^{iv} = 2.82 Å and angle at H8b = 124° for *iv*: 1-x, 2-y, 1-z.

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