Tetrahedron 68 (2012) 10586–10591

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and structural studies of some gold(I) complexes containing selenoureato ligands

Anja Molter [a], Jörg Rust [b], Christian W. Lehmann [b], Fabian Mohr [a,*]

[a] Fachbereich C—Anorganische Chemie, Bergische Universität Wuppertal, Gaussstr. 20, 42119 Wuppertal, Germany
[b] Max-Planck Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form 28 August 2012
Accepted 4 September 2012
Available online 11 September 2012

Keywords:
Acylselenourea
Gold complexes
Soft–soft interactions
X-ray crystal structure

ABSTRACT

N,*N*-Diethyl-*N*′-4-nitrobenzoylselenourea (**HL^{Se}**) reacts with the mono- and dinuclear phosphine gold(I) chloro complexes [AuCl(PR$_3$)] (R=Ph, *o*-tol, Et) and [Au$_2$Cl$_2$(μ-P-P)] (P-P=dppm, dppe, dppp, dppb, dppf) in the presence of base to give gold(I) phosphine selenoureato complexes [Au(L^{Se})(PR$_3$)] [R=Ph (**1**), *o*-tol (**2**), Et (**3**)], [Au$_2$(L^{Se})$_2$(μ-P-P)] [P-P=dppm (**4**), dppe (**5**), dppp (**6**), dppb (**7**), dppf (**8**)] in excellent yields. The compounds were fully characterised by spectroscopic methods and, in the case of compounds **1**, **5** and **8**, by single crystal X-ray diffraction. The compounds consist of a gold atom bound in linear fashion to the phosphine ligand and the selenium atom from the deprotonated acylselenourea. These complexes thus represent the first examples of acylselenoureato metal compounds in which the ligands do not adopt the typical O,Se chelating mode but rather coordinate to the metal only through the selenium atom.

1. Introduction

Acylselenoureas of the type ArC(O)NHC(Se)NR$_2$ derived from the reaction of an aromatic acid chloride with KSeCN and subsequent addition of a secondary amine have been known since 1937.[1] Modified synthetic methods and organic transformations of these (or structurally similar) compounds have been reported since then.[2–9] However, the main focus has been directed towards the use of acylselenoureas as chelating ligands for metal compounds with applications in analytical chemistry, metal extraction and, more recently, as single-source precursors for metal selenide nanomaterials.[10–17] In general, deprotonated acylselenoureas coordinate to a metal centre via both the selenium and oxygen atoms, forming metallacyclic rings (Fig. 1). Numerous examples of such types of compounds with metals including Tl(I), Cd(II), In(III), Zn(II), Ni(II), Co(III), Pb(II), Pd(II) Pt(II) have been reported and many have also been structurally characterised.[2,14–16,18–28]

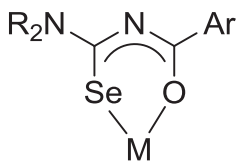


Fig. 1. Schematic representation of a selenoureato metal chelate complex.

It is noteworthy that for the coinage metals (Cu, Ag and Au) only bis(selenoureato) chelate complexes with copper(II) are known.[20,27,29] Given the fact that acylselenoureas contain one hard (oxygen) and one soft (selenium) donor atom, the reaction with a soft metal centre may lead to a compound in which only the selenium is bound to the metal (Fig. 2). In this case however, the stabilizing chelate effect of the selenoureato unit would be lost. It is worth noting, that a gold(I) complex containing an *N*-selenocarbamoyl benzamidine, which can be considered as a nitrogen analogue of a selenourea, was recently isolated and structurally characterized.[30] In this compound the neutral ligand acts as a Se-

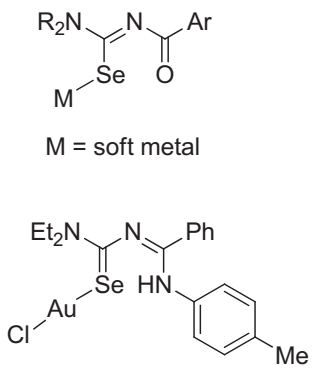


Fig. 2. Schematic representation of a selenoureato complex with a soft metal centre (top) as well as the known gold(I) complex containing a neutral *N*-selenocarbamoyl benzamidine (bottom).

* Corresponding author. E-mail address: fmohr@uni-wuppertal.de (F. Mohr).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.09.023

donor ligand (Fig. 2). There are to date however no examples in the literature of gold complexes containing anionic selenourea derivatives.[31]

Given our past interest in the chemistry of transition metal compounds with chalcogen ligands and the coordination chemistry of organic selenium species,[2,30–48] we wished to study the reactivity of selenoureas with a soft metal centre (gold) to see if either chelate type complexes are formed or if the selenoureato ligand binds only via the selenium atom. The results of this investigation are reported here.

2. Results and discussion

N,*N*-Diethyl-*N*′-4-nitrobenzoylselenourea (**HL^{Se}**) reacts with the phosphine gold(I) chloro complexes [AuCl(PR$_3$)] (R=Ph, *o*-tol, Et) and [Au$_2$Cl$_2$(μ-P-P)] (P-P=dppm, dppe, dppp, dppb, dppf) in the presence of base to give the air- and light-stable gold(I) phosphine selenoureato complexes [Au(L^{Se})(PR$_3$)] [R=Ph (**1**), *o*-tol (**2**), Et (**3**)], [Au$_2$(L^{Se})$_2$(μ-P-P)] [P-P=dppm (**4**), dppe (**5**), dppp (**6**), dppb (**7**), dppf (**8**)] in excellent yields (Scheme 1).

The new compounds were fully characterized by NMR spectroscopy, IR spectroscopy and elemental analysis. The solid-state structures of some compounds were also determined by X-ray crystallography. Most diagnostically, apart from the disappearance of the N–H signal in the proton NMR spectra, are the changes in chemical shifts of the signals in the ^{31}P and ^{77}Se NMR spectra. In the case of the ^{31}P NMR shifts, the singlet resonances are moved several ppm downfield compared to those of the parent chloro complexes. Furthermore, upon deprotonation and coordination to gold the ^{77}Se NMR signal is shifted from 502 ppm in **HL^{Se}** to about 200 pm in the complexes. Although there is not much ^{31}P and ^{77}Se NMR data reported for phosphine gold(I) complexes containing anionic selenium ligands, the trend observed here is consistent with what we have observed previously in gold(I) complexes containing deprotonated selenosemicarbazone ligands.[46] Here too, deprotonation and coordination to gold causes an upfield shift by about 300 pm. While these data do not allow us to unambiguously identify the coordination mode (chelate or monodentate via Se) of the selenoureato unit, comparison of the ^{13}C NMR chemical shifts of the C–O and C–Se signals gives more information. The signal of the C–O carbon atom experiences a much smaller (ca. 5 ppm) shift upon coordination of the acylselenourea unit when compared to **HL^{Se}**. In contrast, that of the C–Se carbon atom shifts by about 12 ppm. In complexes where the selenoureas act as chelating ligands, both C–S and C–O signals experience a shift of ca. 10 ppm when compared to the free ligand. This suggests that the chemical environment about the C–O unit does not change significantly upon coordination and thus the acylselenourea is likely to be bound to gold solely via the selenium atom. Indeed this could be unambiguously confirmed by X-ray crystallographic studies of complexes **1**, **5** and **8**. The molecular structures are shown in Figs. 3–5, selected bond distances and angles are collected in Table 1.

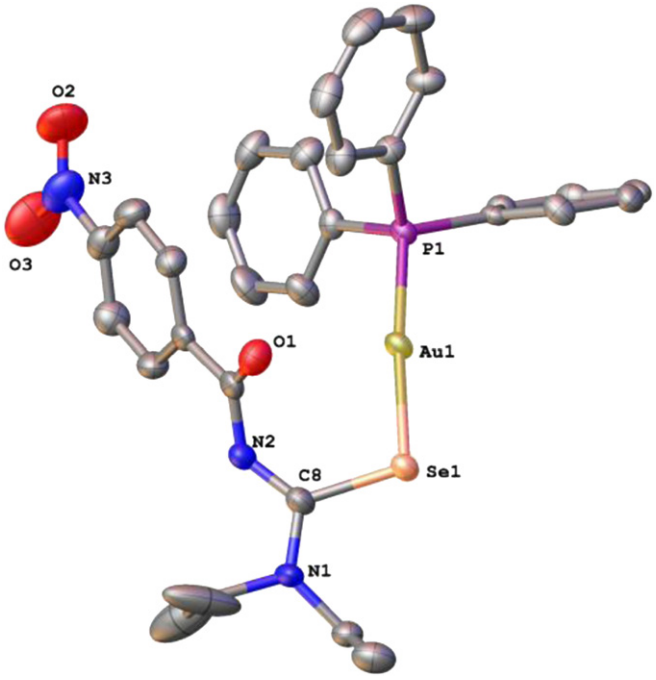
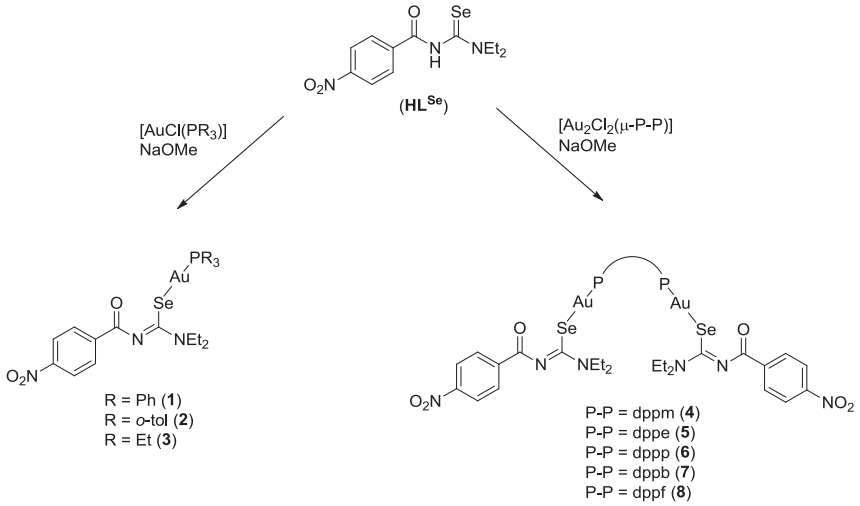


Fig. 3. Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity.

Each compound consists of a gold atom bound, as expected, in linear fashion to a phosphorus atom from the phosphine ligand and the selenium atom from the deprotonated acylselenourea moiety. The Au–P and Au–Se bond distances and angles are within the range typically observed for such compounds.[31] The carbonyl oxygen atom is around 3.4 Å away from the gold atom (sum of the Van der Waals



Scheme 1.

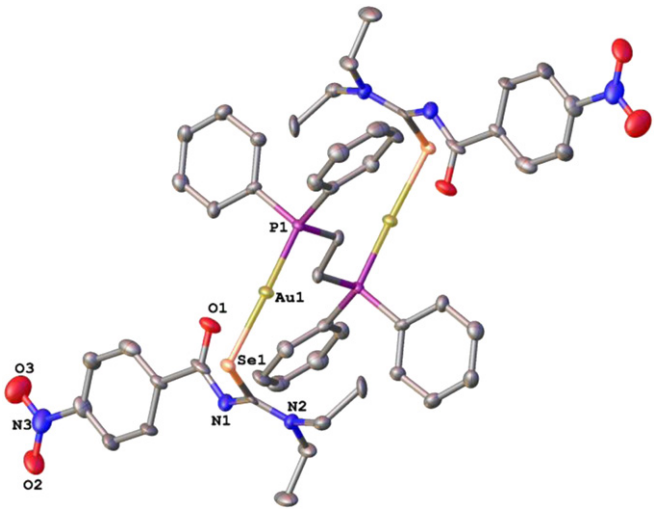


Fig. 4. Molecular structure of complex **5**. Hydrogen atoms have been omitted for clarity.

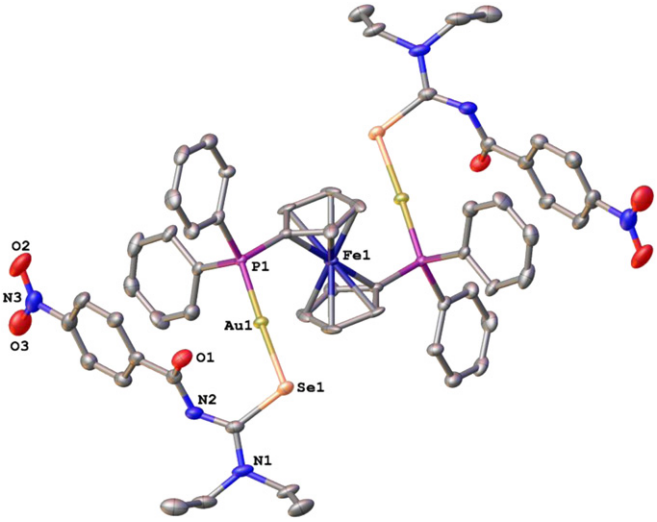


Fig. 5. Molecular structure of complex **8**. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond distances and angles in complexes **1**, **3** and **8**

	[Au(L^{Se})(PPh_3)] (**1**)	[Au_2(L^{Se})$_2$(μ-dppe)] (**5**)	[Au_2(L^{Se})$_2$(μ-dppf)] (**8**)
Bond distances			
P–Au	2.2683(10)	2.262(2)	2.2622(12)
Au–Se	2.4112(4)	2.4170(9)	2.4125(6)
Se–C	1.927(4)	1.968(8)	1.929(6)
O–C	1.240(6)	1.216(10)	1.216(7)
(Se)C–N(C(O))	1.306(6)	1.305(12)	1.318(7)
(O)C–N	1.337(6)	1.354(13)	1.367(7)
(O)C–C(*p*-$C_6H_4NO_2$)	1.503(6)	1.530(12)	1.512(8)
Bond angles			
P–Au–Se	175.31(3)	172.15(6)	177.84.73(8)
Au–Se–C	101.84(13)	94.7(2)	99.85(16)
Se–C–N(C(O))	124.5(3)	120.9(6)	124.0(4)
Se–C–N–C(O)	38.2(6)	44(1)	37.4(8)
O–C–N–C(Se)	30.6(7)	32(2)	24(1)

radii=3.2 Å), too far for any significant interactions to occur. In the structurally related gold(I) chloro compound containing a neutral, S-bonded acylthioureato ligand [AuCl{PhC(O)NHC(S)NEt_2}] the Au–O separation is with 4.2 Å even greater.[49] Comparison of the bond lengths in the ligand backbone also confirms that the degree of delocalization is considerably less than what is usually found in the chelating coordination mode. The C–O bond lengths do not change significantly upon coordination (1.22 vs 1.24 Å), whereas the C–Se distance increases considerably (1.82–1.92 Å). This suggests that the C–Se bond has more single bond character and the C–O bond more double bond character. The lack of delocalization is further confirmed by the C–N bond lengths in the ligand backbone. Whilst in chelate complexes these are almost identical, there is an alternating long, short, long pattern observed in these three complexes. Overall, it can be seen that the deprotonated acylselenoureato ligand coordinates to the gold only via the selenium atom and that the delocalization in the ligand backbone is significantly less than in the chelating coordination mode. These compounds thus represent the first examples of metal compounds containing anionic acylselenoureato ligands, which do not display the chelating coordination mode, which is so typical for this family of ligands. Applications of these compounds in medicine as anti-malaria and anti-tumour agents are currently being investigated by us and results will be reported once they become available.

3. Experimental

3.1. General

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{77}Se NMR spectra were recorded on a Bruker Avance ARX 400 (400 MHz) or Bruker Avance II 600 (600 MHz) spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) and Me_2Se (^{77}Se). Elemental analyses were performed by staff of the micro-analytical laboratory of the University of Wuppertal. Reactions were typically carried out under ambient conditions, without protection from air or moisture. Commercial solvents (HPLC grade) and reagents were used as received. The phosphine gold(I) chloro complexes were readily accessible from the reaction of [AuCl(tht)][50] (tht=tetrahydrothiophene) with the appropriate phosphines in CH_2Cl_2.

3.2. *N,N*-Diethyl-*N′*-4-nitrobenzoylselenourea (HL^{Se})

To a suspension of KSeCN (2.88 g, 20 mmol) and PEG-400 (0.28 mL) in CH_2Cl_2 (10 mL) was added a solution of 4-nitrobenzoylchloride (3.71 g, 20 mmol) in CH_2Cl_2 (20 mL). After ca. 15 min at room temperature Et_2NH (2.07 mL, 20 mmol) was added, and the resulting mixture was stirred for 1 h protected from light. The red-orange mixture was filtered and the filtrate subsequently evaporated to dryness. The resulting solid was recrystallised from EtOH to give 2.29 g (35%) orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.33 (t, J=7.1 Hz, 3H, NCH_2CH_3), 1.41 (t, J=6.3 Hz, 3H, NCH_2CH_3), 3.60 (br s, 2H, NCH_2CH_3), 4.14 (br s, 2H, NCH_2CH_3), 8.03 (d, J=8.2 Hz, 2H, H-2), 8.32 (d, J=8.2 Hz, 2H, H-3), 8.65 (br s, 1H, NH) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ=11.6 (NCH_2CH_3), 12.9 (NCH_2CH_3), 48.6 (NCH_2CH_3), 51.4 (NCH_2CH_3), 124.1 (C-3), 129.1 (C-2), 137.9 (C-1), 150.4 (C-4), 160.4 (C=O), 179.8 (C=Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ=502 ppm. IR (KBr disk) ν: 1347 (*s*, NO_2), 1526 (*s*, NO_2), 1649 (s, C=O amido urea), 2933 (w, C_{sp^3}–H), 2975 (w, C_{sp^3}–H), 3055 (w, C_{sp^2}–H), 3289 (m, N–H) cm^{-1}. Elemental analysis calcd (%) for $C_{12}H_{15}N_3O_3Se$ (328.23 g/mol): C 43.91, H 4.61, N 12.80; found C 43.22, H 4.49, N 13.02.

3.3. Preparation of the gold selenoureato complexes

To a solution of **HL^{Se}** in MeOH was added NaOMe (1.1 equiv). After 15 min of stirring, the phosphine gold chloro complex was

added to the mixture, which was subsequently left to stir at room temperature over night protected from light. Two workup methods were then used:

(A) When the product precipitated out of the reaction mixture, the solid was isolated by filtration, washed with small amounts of methanol, water and diethyl ether and subsequently dried in air.
(B) When a solution formed, this was evaporated to dryness and the residue was dissolved in dichloromethane and passed through Celite. The solution was concentrated and the product precipitated upon addition of a suitable solvent such as diethyl ether, hexane or pentane. The solids were isolated by filtration and subsequently dried in air.

*3.3.1. [Au(L^{Se})(PPh_3)] (**1**).* Workup method B, precipitated with diethyl ether: yellow solid. Yield: 0.124 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.30 (br s, 6H, NCH_2CH_3), 3.77 (br s, 4H, NCH_2CH_3), 7.31–7.36 (m, 12H, *o*-PPh_3, *m*-PPh_3), 7.45 (m, 3H, *p*-PPh_3), 7.74 (d, J=7.7 Hz, 2H, H-3), 7.93 (d, J=8.6 Hz, 2H, H-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=38.1 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.4 (NCH_2CH_3), 45.8 (NCH_2CH_3), 47.9 (NCH_2CH_3), 122.5 (C-3), 129.0 (d, $^3J_{P-C}$=11.5 Hz, *m*-PPh_3), 129.3 (d, $^1J_{P-C}$=56.4 Hz, *i*-PPh_3), 130.0 (C-2), 131.5 (d, $^4J_{P-C}$=2.4 Hz, *p*-PPh_3), 134.0 (d, $^2J_{P-C}$=13.9 Hz, *o*-PPh_3), 144.1 (C-1), 148.5 (C-4), 166.2 (C=O), 168.6 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 236 ppm. IR (KBr disk) ν: 1343 (s, NO_2), 1519 (s, NO_2), 1579 (m, C=O), 2931 (w, C_{sp^3}–H), 2974 (w, C_{sp^3}–H), 3053 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{30}H_{29}N_3AuO_3PSe$ (786.47 g/mol): C 45.81, H 3.72, N 5.34; found: C 46.45, H 3.74, N 5.04.

*3.3.2. Au(L^{Se})P(*o*-tolyl)$_3$] (**2**).* Workup method B, precipitated with diethyl ether: colourless solid. Yield: 0.129 g (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.27 (br s, 6H, NCH_2CH_3), 2.45 (s, 9H, CH_3 P(*o*-tolyl)$_3$), 3.70 (br s, 2H, NCH_2CH_3), 3.81 (br s, 2H, NCH_2CH_3), 6.90 (m, 3H, H-6′ P(*o*-tolyl)$_3$), 7.12 (t, J=7.5 Hz, 3H, H-5′ P(*o*-tolyl)$_3$), 7.25 (t, J=7.0 Hz, 3H, H-3′ P(*o*-tolyl)$_3$), 7.41 (t, J=7.5 Hz, 3H, H-4′ P(*o*-tolyl)$_3$), 7.78 (d, J=8.7 Hz, 2H, H-2), 7.88 (d, J=8.7 Hz, 2H, H-3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=19.7 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.3 (NCH_2CH_3), 23.0 (d, $^3J_{P-C}$=11.1 Hz, CH_3 P(*o*-tolyl)$_3$), 45.5 (NCH_2CH_3), 47.8 (NCH_2CH_3), 122.4 (C-2), 125.6 (d, $^1J_{P-C}$=54.9 Hz, C-1′ P(*o*-tolyl)$_3$), 126.5 (d, $^3J_{P-C}$=9.8 Hz, C-5′ P(*o*-tolyl)$_3$), 129.6 (C-3), 131.5 (d, $^4J_{P-C}$=1.6 Hz, C-4′ P(*o*-tolyl)$_3$), 132.1 (d, $^3J_{P-C}$=8.7 Hz, C-3′ P(*o*-tolyl)$_3$), 133.4 (d, $^2J_{P-C}$=9.3 Hz, C-6′ P(*o*-tolyl)$_3$), 142.9 (d, $^2J_{P-C}$=12.5 Hz, C-2′ P(*o*-tolyl)$_3$), 144.3 (C-1), 148.4 (C-4), 167.5 (C=O), 167.8 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 219 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1519 (s, NO_2), 1579 (m, C=O), 2931 (w, C_{sp^3}–H), 2972 (w, C_{sp^3}–H), 3058 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{33}H_{35}N_3AuO_3PSe$ (828.55 g/mol): C 47.84, H 4.26, N 5.07; found: C 47.38, H 3.93, N 4.84.

*3.3.3. [Au(L^{Se})(PEt_3)] (**3**).* Workup method B, yellow viscous solid. Yield: 0.267 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.84 (dt, $^3J_{H-P}$=18.5 Hz, J=7.6 Hz, 9H, PCH_2CH_3), 1.10 (br s, 6H, NCH_2CH_3), 1.43 (dq, $^2J_{H-P}$=9.8 Hz, J=7.7 Hz, 6H, PCH_2), 3.51 (br s, 2H, NCH_2CH_3), 3.64 (br s, 2H, NCH_2CH_3), 8.01 (d, J=9.0 Hz, 2H, H-3), 8.06 (d, J=9.0 Hz, 2H, H-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=35.9 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=8.2 (PCH_2CH_3), 12.7 (NCH_2CH_3), 12.9 (NCH_2CH_3), 17.2 (d, $^1J_{P-C}$=32.7 Hz, PCH_2CH_3), 45.0 (br s, NCH_2CH_3), 47.6 (br s, NCH_2CH_3), 122.3 (C-3), 129.8 (C-2), 144.1 (C-1), 148.3 (C-4), 166.6 (C=O), 167.1 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 242 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1519 (s, NO_2), 1576 (m, C=O), 2932 (m, C_{sp^3}–H), 2967 (m, C_{sp^3}–H), 3068 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{18}H_{29}N_3AuO_3PSe$ (642.34 g/mol): C 33.66, H 4.55, N 6.54; found: C 34.08, H 4.88, N 6.61.

*3.3.4. [Au_2(L^{Se})$_2$(μ-dppm)] (**4**).* Workup method B, precipitated with diethyl ether: yellow solid. Yield: 0.137 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.30 (br s, 12H, NCH_2CH_3), 3.07 (ABX-t, 2H, PCH_2), 3.66 (br s, 4H, NCH_2CH_3), 3.92 (br s, 4H, NCH_2CH_3), 7.19 (m, 8H, *m*-PPh_2), 7.29–7.41 (m, 12H, *o*-PPh_2, *p*-PPh_2), 7.66 (d, J=7.4 Hz, 4H, H-2), 7.84 (d, J=8.2 Hz, 4H, H-3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=30.1 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.2 (br s, NCH_2CH_3), 29.5 (ABX-t, PCH_2), 46.0 (br s, NCH_2CH_3), 48.3 (br s, NCH_2CH_3), 122.4 (C-2), 128.2 (m, *i*-PPh_2), 129.0 (ABX-t, *m*-PPh_2), 129.9 (C-3), 131.8 (*p*-PPh_2), 133.2 (ABX-t, *o*-PPh_2), 143.8 (C-1), 148.4 (C-4), 163.2 (C=O), 166.7 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 277 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1518 (s, NO_2), 1569 (s, C=O), 2931 (w, C_{sp^3}–H), 2973 (w, C_{sp^3}–H), 3052 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{49}H_{50}N_6Au_2O_6P_2Se_2$ (1432.76 g/mol): C 41.08, H 3.52, N 5.87; found: C 40.91, H 3.15, N 6.03.

*3.3.5. [Au_2(L^{Se})$_2$(μ-dppe)] (**5**).* Workup method B, precipitated with methanol: yellow solid. Yield: 0.167 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.31 (br s, 12H, NCH_2CH_3), 2.66 (s, 4H, PCH_2), 3.79 (br s, 8H, NCH_2CH_3), 7.35 (t, J=7.3 Hz, 8H, *m*-PPh_2), 7.44 (t, J=7.3 Hz, 4H, *p*-PPh_2), 7.55 (t, J=6.1 Hz, 8H, *o*-PPh_2), 7.79 (d, J=8.4 Hz, 4H, H-2), 7.88 (d, J=8.5 Hz, 4H, H-3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=37.3 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.4 (NCH_2CH_3), 23.7 (ABX-t, PCH_2), 47.9 (NCH_2CH_3), 122.7 (C-2), 128.7 (m, *i*-PPh_2), 129.2 (ABX-t, *m*-PPh_2), 129.9 (C-3), 131.9 (*p*-PPh_2), 133.3 (ABX-t, *o*-PPh_2), 144.0 (C-1), 148.7 (C-4), 164.3 (C=O), 168.7 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 231 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1518 (s, NO_2), 1582 (s, C=O), 2932 (m, C_{sp^3}–H), 2964 (m, C_{sp^3}–H), 3058 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{50}H_{52}N_6Au_2O_6P_2Se_2$ (1446.79 g/mol): C 41.51, H 3.62, N 5.81; found: C 41.29, H 3.46, N 5.68.

*3.3.6. [Au_2(L^{Se})$_2$(μ-dppp)] (**6**).* Workup method B, precipitated with hexane: yellow solid. Yield: 0.130 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.31 (br s, 12H, NCH_2CH_3), 1.71 (m, 2H, CH_2), 2.57 (s, 4H, PCH_2), 3.77 (br s, 8H, NCH_2CH_3), 7.34 (dt, J=7.5, 1.7 Hz, 8H, *m*-PPh_2), 7.34 (m, 4H, *p*-PPh_2), 7.50 (m, 8H, *o*-PPh_2), 7.82 (br s, 4H, H-2), 7.88 (br s, 4H, H-3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=31.6 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.3 (NCH_2CH_3), 19.5 (m, CH_2), 28.3 (dd, $^1J_{P-C}$=33.6 Hz, $^3J_{P-C}$=11.5 Hz, PCH_2), 46.0 (br s, NCH_2CH_3), 48.2 (br s, NCH_2CH_3), 122.7 (C-2), 129.1 (d, $^3J_{P-C}$=11.3 Hz, *m*-PPh_2), 129.2 (d, $^1J_{P-C}$=54.2 Hz, *i*-PPh_2), 130.0 (C-3), 131.6 (d, $^4J_{P-C}$=2.3 Hz, *p*-PPh_2), 133.2 (d, $^2J_{P-C}$=13.4 Hz, *o*-PPh_2), 143.8 (C-1), 148.7 (C-4), 166.0 (C=O), 167.9 (C–Se) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): 242 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1519 (s, NO_2), 1569 (s, C=O), 2930 (w, C_{sp^3}–H), 2972 (w, C_{sp^3}–H), 3052 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{51}H_{54}N_6Au_2O_6P_2Se_2$ (1460.81 g/mol): C 41.93, H 3.73, N 5.75; found: C 41.69, H 3.77, N 5.88.

*3.3.7. [Au_2(L^{Se})$_2$(μ-dppb)] (**7**).* Workup method A: yellow solid. Yield: 0.118 g (34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.31 (br s, 12H, NCH_2CH_3), 1.60 (m, 2H, CH_2), 2.18 (s, 4H, PCH_2), 3.68 (br s, 4H, NCH_2CH_3), 3.90 (br s, 4H, NCH_2CH_3), 7.34–7.44 (m, 8H, *m*-PPh_2), 7.41–7.48 (m, 12H, *p*-PPh_2, *o*-PPh_2), 7.89 (d, J=7.8 Hz, 4H, H-2), 7.97 (d, J=8.5 Hz, 4H, H-3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=34.6 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=13.1 (NCH_2CH_3), 26.5 (dd, $^2J_{P-C}$=18.0 Hz, $^3J_{P-C}$=4.3 Hz, PCH_2CH_2), 27.8 (d, $^1J_{P-C}$=34.1 Hz, PCH_2), 46.2 (br s, NCH_2CH_3), 48.7 (br s, NCH_2CH_3), 122.8 (C-2), 129.0 (d, $^3J_{P-C}$=11.5 Hz, *m*-PPh_2), 129.3 (*i*-PPh_2), 129.9 (C-3), 131.5 (*p*-PPh_2), 133.5 (d, $^2J_{P-C}$=13.5 Hz, *o*-PPh_2), 142.9 (C-1), 148.9 (C-4), 164.3 (C=O), 166.7 (C–Se) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): 240 ppm. IR (KBr disk) ν: 1343 (s, NO_2), 1519 (s, NO_2), 1583 (s, C=O), 2930 (m, C_{sp^3}–H), 2974 (m, C_{sp^3}–H), 3054 (w, C_{sp^2}–H)

cm^{-1}. Elemental analysis, calcd (%) for $C_{52}H_{56}N_6Au_2O_6P_2Se_2$ (1474.84 g/mol): C 42.35, H 3.83, N 5.70; found: C 41.27, H 3.81, N 5.38.

*3.3.8. [$Au_2(L^{Se})_2(\mu$-dppf)] (**8**).* Workup method A: yellow solid. Yield: 0.158 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.30 (br s, 12H, NCH_2CH_3), 3.76 (br s, 8H, NCH_2CH_3), 4.21 (s, 4H, H-2′, PC_5H_4), 4.60 (s, 4H, H-3′, PC_5H_4), 7.29–7.35 (m, 16H, *o*-PPh_2, *m*-PPh_2), 7.40–7.43 (m, 4H, *p*-PPh_2), 7.80 (d, J=8.6 Hz, 4H, H-2), 7.94 (d, J=8.6 Hz, 4H, H-3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=32.8 ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ=13.5 (NCH_2CH_3), 45.8 (NCH_2CH_3), 47.8 (NCH_2CH_3), 72.1 (d, $^1J_{P-C}$=65.0 Hz, C-1′, PC_5H_4), 74.7 (d, $^3J_{P-C}$=8.1 Hz, C-3′, PC_5H_4), 74.8 (d, $^2J_{P-C}$=12.9 Hz, C-2′, PC_5H_4), 122.6 (C-2), 128.7 (d, $^3J_{P-C}$=11.6 Hz, *m*-PPh_2), 130.0 (C-3), 130.6 (d, $^1J_{P-C}$=57.5 Hz, *i*-PPh_2), 131.3 (d, $^4J_{P-C}$=2.2 Hz, *p*-PPh_2), 133.4 (d, $^2J_{P-C}$=14.1 Hz, *o*-PPh_2), 144.1 (C-1), 148.6 (C-4), 165.8 (C=O), 168.4 (C–Se) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): 235 ppm. IR (KBr disk) ν: 1342 (s, NO_2), 1519 (s, NO_2), 1574 (m, C=O), 2930 (w, C_{sp^3}–H), 2974 (w, C_{sp^3}–H), 3052 (w, C_{sp^2}–H) cm^{-1}. Elemental analysis, calcd (%) for $C_{58}H_{56}N_6Au_2FeO_6P_2Se_2$ (1602.75 g/mol): C 43.46, H 3.52, N 5.24; found: C 43.31, H 3.45, N 5.24.

3.4. X-ray crystallography

Crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a saturated dichloromethane solution of the complex **1**, **5** or **8**, respectively. Diffraction data for compounds **1** and **5** were collected using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. For the data collection the Mo source emitting graphite-monochromated Mo Kα radiation (λ=0.71073 Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package.[51] Diffraction data for compound **8** were collected at 100 K using a Nonius KappaCCD diffractometer with a rotating anode (Nonius FR591) producing Mo Kα-radiation (λ=0.71073 Å) equipped with a graphite monochromator. Data collection and integration were controlled by the collect package.[52] Scaling and absorption correction were performed using SADABS.[53] The structures were solved using Direct Methods or Patterson Methods and refined by Full-Matrix-Least-Squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program Olex2.[54] Important crystallographic and refinement parameters are collected in Table 2. The data set for **1** contained residual electron density due to severely disordered solvent molecules. After many unsuccessful attempts at modelling this disorder, the SQUEEZE algorithm within PLATON was applied.[55]

Table 2
Crystallographic and refinement details for complexes **1**, **5** and **8**

	[Au(L^{Se})(PPh_3)] (**1**)	[$Au_2(L^{Se})_2$(μ-dppe)] (**5**)	[$Au_2(L^{Se})_2$(μ-dppf)] (**8**)
Empirical formula	$C_{30}H_{29}AuN_3O_3PSe$	$C_{50}H_{52}Au_2N_6O_6P_2Se_2$	$C_{58}H_{56}N_6Au_2FeO_6P_2Se_2$
Molecular weight (g mol^{-1})	786.46	1446.77	1602.73
Crystal colour and shape	Yellow block	Yellow block	Yellow block
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	*C*2/*c*
a (Å)	27.3351(6)	8.6513(19)	26.229(4)
b (Å)	8.56693(19)	10.8626(11)	8.4240(14)
c (Å)	26.8640(5)	15.3145(13)	26.765(4)
α (°)		74.369(8)	
β (°)	94.6948(19)	88.486(11)	94.579(3)
γ (°)		66.708(15)	
V (Å^3)	6269.9(2)	1267.8(3)	5894.8(17)
T (K)	150	130	100
Z	8	1	4
Calcd density (g cm^{-3})	1.666	1.895	1.806
Crystal size (mm^3)	0.1×0.05×0.03	0.38×0.22×0.06	0.08×0.06×0.02
μ (mm^{-1})	5.938	7.333	6.551
2Θ range (°)	5.90–58.66	7.04–58.80	3.06–59.50
No. of data collected	18,782	10,888	73,964
No. of unique data	7345[*R*(int)=0.0276]	5818[*R*(int)=0.0737]	8378[*R*(int)=0.1078]
R_1^a [$F^2>2\sigma(F^2)$]	0.0334	0.0602	0.0368
wR_2^b (all data)	0.0708	0.1502	0.1102
S^c (all data)	1.058	1.039	1.030
Largest diff. peak/hole (e Å^{-3}) min/max	1.4/−1.3	3.8/−5.2	1.6/−2.2

Acknowledgements

A.M. thanks the University of Wuppertal for a scholarship. We gratefully acknowledge a generous donation of selenium metal from Retorte GmbH.

References and notes

1. Douglass, I. B. *J. Am. Chem. Soc.* **1937**, *59*, 740–742.
2. Molter, A.; Rust, J.; Lehmann, C. W.; Mohr, F. *Arkivoc* **2011**, *vi*, 10–17.
3. Wei, T. B.; Wang, H.; Lin, Q.; Zhang, Y. M. *Chin. J. Org. Chem.* **2005**, *28*, 1565–1569.
4. Wei, T. B.; Wang, H.; Lin, Q.; Zhang, Y. M. *Chem. J. Chin. Univ.* **2006**, *27*, 1680–1682.
5. Koketsu, M.; Yamamura, Y.; Aoki, H.; Ishihara, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2006**, *181*, 2699–2708.
6. Zhou, Y.; Heimgartner, H. *Helv. Chim. Acta* **2000**, *83*, 539–553.
7. Köhler, R.; Beyer, L.; Moll, M. *Tetrahedron* **1990**, *46*, 7735–7738.
8. Weber, G.; Hartung, J.; Beyer, L. *Tetrahedron Lett.* **1988**, *29*, 3475–3476.
9. Liebscher, J.; Hartmann, H. *Z. Chem.* **1976**, *16*, 18–19.
10. Beyer, L.; Kirmse, R.; Hoyer, E. *Z. Chem.* **1975**, *15*, 197.
11. Shome, S. C.; Mazumdar, M.; Das, S. K. *J. Indian Chem. Soc.* **1980**, *57*, 69–72.
12. Schuster, M.; König, K. H. *Fresenius Z. Anal. Chem.* **1987**, *327*, 102–104.
13. Schuster, M.; König, K. H. *Fresenius Z. Anal. Chem.* **1988**, *331*, 383–386.
14. Bruce, J. C.; Revaprasadu, N.; Koch, K. R. *New J. Chem.* **2007**, *31*, 1647–1653.
15. Akhtar, J.; Mehmood, R. F.; Malik, M. A.; Iqbal, N.; O'Brien, P.; Raftery, J. *Chem. Commun.* **2011**, 1899–1901.
16. Akhtar, J.; Malik, M. A.; Stubbs, S. K.; O'Brien, P.; Helliwell, M.; Binks, D. J. *Eur. J. Inorg. Chem.* **2011**, 2984–2990.
17. Akhtar, J.; Akhtar, M.; Malik, M. A.; O'Brien, P.; Raftery, J. *J. Am. Chem. Soc.* **2012**, *134*, 2485–2487.
18. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1689–1692.
19. Schuster, M.; Bensch, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 737–742.
20. Kampf, M.; Richter, R.; Hennig, L.; Eidner, A.; Baldamus, J.; Kirmse, R. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2677–2686.
21. Kampf, M.; Richter, R.; Gerber, S.; Kirmse, R. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1437–1443.
22. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 791–795.
23. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 786–790.
24. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1994**, *620*, 177–182.
25. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1479–1482.
26. Schuster, M.; Bensch, W. *Z. Naturforsch.* **1994**, *49b*, 1615–1619.
27. Kampf, M.; Richter, R.; Griebel, J.; Weller, A.; Kirmse, R. *Z. Anorg. Allg. Chem.* **2005**, *631*, 698–708.
28. Bruce, J. C.; Koch, K. R. *Acta Crystallogr.* **2008**, *C64*, m1–m4.
29. Kirmse, R.; Beyer, L.; Hoyer, E. *Chem. Phys. Lett.* **1977**, *49*, 544–546.
30. Bredenkamp, A.; Zeng, X.; Mohr, F. *Polyhedron* **2012**, *33*, 107–113.
31. Molter, A.; Mohr, F. *Coord. Chem. Rev.* **2010**, *254*, 19–45.
32. Vergara, E.; Miranda, S.; Mohr, F.; Cerrada, E.; Tiekink, E. R. T.; Romero, P.; Laguna, M. *Eur. J. Inorg. Chem.* **2007**, 2926–2933.
33. Dolfen, D.; Schottler, K.; Seied-Mojtaba, V.; Jakupec, M. A.; Keppler, B. K.; Tiekink, E. R. T.; Mohr, F. *J. Inorg. Biochem.* **2008**, *102*, 2067–2071.
34. Gallenkamp, D.; Tiekink, E. R. T.; Mohr, F. *Phosphorus, Sulfur Silicon* **2008**, *183*, 1050–1056.
35. Miranda, S.; Vergara, E.; Mohr, F.; de Vos, D.; Cerrada, E.; Mendía, A.; Laguna, M. *Inorg. Chem.* **2008**, *47*, 5641–5648.
36. Alagöz, C.; Brauer, D. J.; Mohr, F. *J. Organomet. Chem.* **2009**, *694*, 1283–1288.
37. Fuge, F.; Lehmann, C.; Mohr, F. *J. Organomet. Chem.* **2009**, *694*, 2395–2401.
38. Gallenkamp, D.; Porsch, T.; Molter, A.; Tiekink, E. R. T.; Mohr, F. *J. Organomet. Chem.* **2009**, *694*, 2380–2385.
39. *Gold Chemistry. Applications and Future Directions in the Life Sciences*; Mohr, F., Ed.; Wiley-VCH: Weinheim, 2009.
40. Schuh, E.; Valiahdi, S. M.; Jakupec, M. A.; Keppler, B. K.; Chiba, P.; Mohr, F. *Dalton Trans.* **2009**, 10841–10845.
41. Ben Dahman Andaloussi, M.; Mohr, F. *J. Organomet. Chem.* **2010**, *695*, 1276–1280.
42. Bippus, P.; Molter, A.; Müller, D.; Mohr, F. *J. Organomet. Chem.* **2010**, *695*, 1657–1662.
43. Pisiewicz, S.; Rust, J.; Lehmann, C. W.; Mohr, F. *Polyhedron* **2010**, *29*, 1968–1972.

44. Bippus, P.; Skocic, M.; Jakupec, M. A.; Keppler, B. K.; Mohr, F. *J. Inorg. Biochem.* **2011**, *105*, 462–466.
45. Molter, A.; Mohr, F. *Dalton Trans.* **2011**, *40*, 3754–3758.
46. Molter, A.; Rust, J.; Lehmann, C. W.; Deepa, G.; Chiba, P.; Mohr, F. *Dalton Trans.* **2011**, *40*, 9810–9820.
47. Molter, A.; Bill, E.; Mohr, F. *Inorg. Chem. Commun.* **2012**, *17*, 124–127.
48. Schuh, E.; Pflüger, C.; Citta, A.; Folda, A.; Rigobello, M. P.; Bindoli, A.; Casini, A.; Mohr, F. *J. Med. Chem.* **2012**, *55*, 5518–5528.
49. Bensch, W.; Schuster, M. *Z. Anorg. Allg. Chem.* **1992**, *611*, 99–102.
50. Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85–91.
51. CrysAlis Pro 171.33.49; Oxford Diffraction: Oxford, UK, 2009.
52. COLLECT, data Collection Software; Nonius BV: Delft, NL, 1999.
53. SMART Version 6.24; Bruker AXS: Madison, WI, 1997.
54. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
55. Spek, A. L. *Acta Cystallogr.* **1990**, *A46*, C34.