Correspondence to:
Professor W. Henderson,
Department of Chemistry,
University of Waikato,
Private Bag 3105,
Hamilton,
New Zealand
e-mail w.henderson@waikato.ac.nz
FAX 0064-7-838-4219

Cycloaurated triphenylphosphine-sulfide and -selenide

Kelly J. Kilpin, William Henderson* and Brian K. Nicholson*

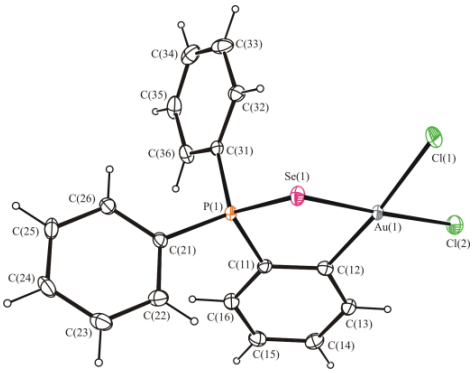
Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received:

Synopsis

Cycloaurated $Ph_3P{=}S$ and $Ph_3P{=}Se$ were synthesised by transmetallation reactions from 2-$Hg[(C_6H_4)P(E)Ph_2]_2$ (E = S or Se) or 2-$HgCl[(C_6H_4)P(E)Ph_2]$; $PhP(S)(NEt_2)_2$ was also cycloaurated *via* transmetallation reaction.

Graphic for synopsis



Abstract

The first examples of cycloaurated phosphine sulfides and triphenylphosphine selenide have been synthesised; these complexes are fairly rare examples of gold(III) complexes with potentially reducing sulfur- and selenium-donor ligands. The cycloaurated complex (2-$AuCl_2C_6H_4$)$P(S)Ph_2$ was synthesised in good yield by transmetallation of the organomercury precursor 2-$Hg(C_6H_4P(S)Ph_2)_2$ with $Me_4N[AuCl_4]$. A route to the chloro-mercury analogue 2-($ClHgC_6H_4$)$P(S)Ph_2$ was developed by reaction of the cyclomanganated triphenylphosphine sulfide (2-$(Mn(CO)_4)C_6H_4$)$P(S)Ph_2$ with $HgCl_2$; this mercury substrate was also used in the sysnthesis of (2-$AuCl_2C_6H_4$)$P(S)Ph_2$. The cycloaurated triphenylphosphine selenide complex (2-$AuCl_2C_6H_4$)$P(Se)Ph_2$ was synthesised by an analogous methodology using the new phosphine selenide 2-$Hg(C_6H_4P(Se)Ph_2)_2$ [prepared from 2-$Hg(C_6H_4PPh_2)_2$ and elemental Se under sonication]. The phosphonamidic analogue (2-$AuCl_2C_6H_4$)$P(S)(NEt_2)_2$ has also been synthesised from $PhP(S)(NEt_2)_2$ *via* lithiation and mercuration. X-ray crystal structures of several compounds are reported, and show the presence of puckered ring systems.

Keywords: Gold complexes; Cyclometallated ligands; Phosphine chalcogenides; X-ray crystal structure; Organomercury compounds

Introduction

Coordination compounds of tertiary phosphine chalcogenides are well known and a number of reviews are dedicated to complexes with either the oxygen, sulfur or selenium atom of the ligand acting as a neutral η^1 donor to the metal centre.[1,2] $Ph_3P{=}O$[3,4,5] (a hard donor ligand) and $Ph_3P{=}S$[3-5, 6] (a soft donor ligand) both form complexes with Au(III) (a soft metal centre) *via* the electron-rich chalcogen atom. Very recently, the cycloaurated phosphine oxide derivative **1** was prepared by transmetallation of the corresponding methyltin derivatives **2**.[7] Cycloaurated complexes have been attracting considerable interest, primarily as a result of the redox-stabilisation of the Au(III) centre imparted by the metallacyclic structure.[8] However, the majority of cycloaurated complexes involve C,N chelates, and we are unaware of any examples of cycloaurated phosphine-sulfides (C,S donors) or –selenides (C,Se donors). Complex **1** appears to be the sole example to date of a C,O cycloaurated system.

Complexes containing *ortho*-metallated phosphine chalcogenide ligands are themselves surprisingly rare in the literature. The series of *ortho*-manganated complexes of $Ph_3P{=}O$ (**3a**), $Ph_3P{=}S$ (**3b**) and $Ph_3P{=}Se$ (**3c**) has been studied;[9] yields of the sulfide complex **3c** were excellent (90%) but both the selenide **3c** (22%) and the oxide **3a** (41%) were only obtained in moderate yields because of either the instability of the P=Se bond or the unfavourable bond angle that is formed at the oxygen in the cyclometallated complex. The tin complex **4** was synthesised by reaction of the free ligand with Ph_3SnCl *via* an *ortho*-lithiated intermediate. The resulting complex had weak O-Sn and S-Sn interactions both in the solid state and in solution. However, the cationic complex **5**, formed by the reaction of **4** with $CPh_3^+PF_6^-$, had much stronger O-Sn and S-Sn interactions;[10] stannated $Ph_3P{=}O$ **6** has been synthesised indirectly.[11] With the exception of the Pt(II) and Pd(II) compounds (**7**) containing tridentate

S,C,S' pincer ligands,[12] a selection of indirectly synthesised Pt(IV)[13] (**8** and **9**) and Rh[14] (**10**) compounds containing cyclometallated $Ph_3P{=}O$ moieties, and *ortho*-mercurated $Ph_3P{=}O$ and $Ph_3P{=}S$,[15,16] cyclometallated complexes of the heavier transition metal elements have thus far been largely neglected.

Results and discussion

Synthesis and characterisation of organomercury precursors

Cycloaurated complexes are typically synthesised either by direct C-H bond activation of the ligand by *e.g.* $H[AuCl_4]$, or by transmetallation, often from the corresponding *ortho*-mercurated compound.[8] For phosphine chalcogenide ligands direct cyclometallation with gold was not possible, because of reduction of the gold(III), so the transmetallation route from the *ortho*-mercurated complexes was employed. Synthesis of *ortho*-mercurated complexes is commonly achieved by either direct mercuration of the substrate or transmetallation reactions from *ortho*-lithiated or Grignard intermediates, with the choice of method often limited by the functional groups present on the ligand.[17]

Bennett *et al*. have shown that the *ortho*-mercurated bisphosphine complex **11** reacts with either hydrogen peroxide or sulfur to yield the bisphosphine-dioxide **12a** or -disulfide **12b** respectively.[15,16] Identifying these compounds as suitable cycloauration substrates, we extended this series of compounds to the diselenide analogue **12c** by reaction of **11** with (grey) selenium powder under ultrasonic conditions. The use of ultrasound allows the use of shorter reaction times and lower reaction temperatures than with the more traditional thermal route, *e.g.* using selenium in refluxing toluene.[18] The selenide **12c** is a white, air-stable solid and its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 41.4 ppm with the expected coupling to

both ^{199}Hg (284 Hz) and ^{77}Se (684 Hz). Electrospray ionisation mass spectrometry (ESI MS) confirmed that both phosphine groups had been converted to the corresponding selenide, however ions due to mixed oxide/selenide species were also present. As only one compound was observed in the $^{31}P\{^{1}H\}$ NMR spectrum it is possible that loss of selenium and subsequent oxidation is occurring inside the spectrometer. Alternatively, if very small traces of the mixed oxide/selenide species were present in the sample then they would be likely to have a higher proton affinity and therefore ionise more efficiently than **12c**. Addition of $AgNO_3$ solution to **12c** prior to ESI MS analysis resulted in silver adducts in the spectrum (*e.g.* [**12**+Ag]$^+$), however the mixed oxide/selenide species was still present. We have previously used silver ions to successfully derivatise (poorly-ionising) phosphine and phosphine chalcogenide compounds for ESI MS analysis.[19,20,21]

Organo-manganese reagents provide an alternative pathway to *ortho*-mercurated precursors not accessible by traditional routes.[22] For example, reaction of *ortho*-manganated acetophenone **13** with $HgCl_2$ yielded the *ortho*-mercurated derivative **14**, a compound that cannot be formed by the classical methods of mercuration.[23] The use of lithium or Grignard reagents is excluded because of the ketone functionality and direct mercuration occurs at the methyl carbon (as a result of keto-enol tautomerisation). *Ortho*-manganated $Ph_3P{=}S$ **3b** can be synthesised in high yields (*ca.* 90%) by reaction of $Ph_3P{=}S$ with $PhCH_2Mn(CO)_5$[9] so we investigated whether transmetallation from **3b** would produce *ortho*-mercurated triphenylphosphine sulfide **15**. Indeed, the desired compound is formed cleanly and in high yield upon refluxing **3b** with a slight excess of $HgCl_2$ in methanol (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectrum of **15** (in $CDCl_3$) has a single peak at 48.2 ppm, which is close to the literature value of the bis-phosphine sulfide **12b** (47.7 ppm, acquired in CD_2Cl_2).[16]

ESI MS of **15** shows ions $[M+H]^+$, $[M+Na]^+$ and $[2M\text{-}Cl]^+$; it also indicated that the diarylmercury complex **12b** had also been formed (by an ion at *m/z* 789.093 corresponding to

[**12b**+H]$^+$, 100%), so an X-ray crystal structure was performed in order to unequivocally characterise the compound. The molecular structure and the atom labelling scheme are shown in Figure 1 and selected bond lengths and angles in Table 1. The mercury atom is bonded to the *ortho* carbon of one of the phenyl rings, confirming transmetallation from manganese. In other structurally characterised complexes where tertiary phosphine sulfides are coordinated to Hg(II) the S-Hg bond lengths range from 2.500 Å to 2.761 Å, and the P-S-Hg angles are in the range of 99.31-110.99°.[24,25] The P-S-Hg angle in **15** (86.58°) is extremely acute; most P-S-M angles in coordinated phosphine sulfides fall within the range of 102-116° (see Table 3). The P(1)-S(1) bond length in **15** [1.9745(11) Å] is longer than in Ph_3P=S (1.950 Å),[26] and the coordination around the mercury atom deviates slightly from linear geometry [C(12)-Hg(1)-Cl(1) angle 173.34(9)°]. These observations indicate that the interaction between the mercury and sulfur [Hg(1)···S(1) 2.9585(8) Å] is substantial enough to hold the compound in a *pseudo*-cyclic structure.

The *ortho*-mercurated thiophosphonamidic compound **16** was also prepared from $PhP(S)(NEt_2)_2$ and investigated as a cycloauration substrate. Craig *et al*.[27] have previously shown that the methyl analogue $PhP(S)(NMe_2)_2$ undergoes *ortho*-lithiation on the phenyl ring; the commercially available ethyl analogue behaves in an identical manner and the resulting *ortho*-lithiated compound can be further reacted with $HgCl_2$ to give **16** in good yield. Like **15**, there is a peak in the mass spectrum (*m/z* 769.266) corresponding to the diaryl mercury complex [2-Hg($C_6H_4P(S)(NEt_2)_2)_2$+H]$^+$. However, the $^{31}P\{^1H\}$ NMR spectrum shows a ^{31}P-^{199}Hg coupling of 414 Hz, very similar to the coupling seen in **15**. Microelemental analysis also supports the structure being the mercury chloride species **16**.

Synthesis of cycloaurated phosphine chalcogenides

The synthetic reactions are summarised in Scheme 2. The cycloaurated triphenylphosphine sulfide complex **17b** was obtained by reaction of the *ortho*-mercurated phosphine sulfide complexes **12b** and **15** with $[Me_4N][AuCl_4]$ and $[Me_4N]Cl$ in acetonitrile. The cycloaurated triphenylphosphine selenide complex **17c** was likewise formed from the organomercury reagent **12c**. When the donor atom was selenium, the transmetallation reaction proceeded in three hours compared to the 24 hours required with the sulfur donor. Both **17b** and **17c** are yellow microcrystalline compounds, however **17c** appears to be moisture sensitive and when isolated in the solid form it decomposes over time (even in darkness) to give a black powder. Complex **16** also readily transmetallates in an analogous manner; when reacted with $[Me_4N][AuCl_4]$ the cycloaurated complex **18** was isolated as a fluffy pale-yellow solid. All of the transmetallation reactions gave adequate to good yields of cycloaurated product.

Attempts at synthesising cycloaurated $Ph_3P{=}O$ *via* transmetallation from **12a** were unsuccessful, the same synthetic methodology as for **12b** and **12c** giving a variety of unidentified compounds observed by $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixture. Longer reaction times and changing the solvent from acetonitrile to DMSO resulted in complete loss of **12a** and evidence of the cycloaurated product in ESI mass spectrometry, but, despite numerous attempts, we were unable to isolate **12a**, which would be analogous to the recently reported derivative **1**.

X-ray crystal structures of 2-$AuCl_2(C_6H_4)P(S)Ph_2$ 17b, 2-$AuCl_2(C_6H_4)P(Se)Ph_2$ 17c and 2-$AuCl_2(C_6H_4)P(S)(NEt_2)_2$ 18

X-ray crystal structure analyses of **17b** and **17c** showed that the compounds are iso-structural and isomorphous. The molecular structure and atom numbering scheme of the selenide are shown in Figure 2, with important bond parameters for both structures presented in Table 2; the numbering scheme for the sulfide corresponds to that of the selenide. In each case, a new five-membered metallacyclic ring has formed with the gold bonded in the *ortho* position of one of the phenyl rings and either a sulfur or a selenium atom as the neutral donor. Two chloride ligands complete the essentially square planar coordination geometry around the metal. The greatest deviations from the gold coordination planes are 0.0681(14) Å (C12) for **17b** and 0.0643(8) Å (C12) for **17c**. Because of the greater *trans* influence of the carbon-bonded phenyl ring, the Au(1)-Cl(1) bonds in **17b** and **17c** [2.3635(11) and 2.3628(6) Å respectively] are longer than the Au(1)-Cl(2) bonds [2.3094(12) and 2.3222(6) Å] *trans* to the chalcogen. The Au-Cl bond *trans* to the selenium atom [2.3222(6) Å] is longer than the Au-Cl bond *trans* to the sulfur atom [2.3094(12) Å] indicating a greater *trans* influence of the P=Se group.

Coordination to the metal lengthens the P=E bond, from 1.950(3) Å in $Ph_3P{=}S$[26] to 2.0324(16) Å in **17b**, and from 2.112(1) Å in $Ph_3P{=}Se$[28] to 2.1839(6) in **17c**. The Au-S bond [2.3073(11) Å] is comparable with other Au(III)-S bond lengths where the sulfur originates from a tertiary phosphine sulfide group.[29,30] Likewise, the Au-Se bond in **17c** is comparable with similar complexes[31] and in conjunction with the P-Se bond length suggests a strong gold-selenium interaction. The bite angle of the ligand is close to 90° for both **17b** and **17c**. The metallacyclic rings of both complexes are significantly puckered, which contrasts to the *ortho*-manganated analogues **3b** and **3c**, where the metallacyclic rings are planar. The greatest

deviations from the mean metallacyclic plane are P(1) [+0.3002(14) Å] and S(1) [-0.3016(11) Å] for **17b** and P(1) [+0.3114(8)] and Se(1) [-0.2976(6) Å] for **17c**.

Table 3 summarises a review of the Cambridge Crystallographic Database for structures of triphenylphosphine chalcogenide ligands where the chalcogenide atom acts as an η^1 donor.[32] In these complexes the chalcogenide atom is not constrained so the intrinsically preferred geometry around the chalcogenide atom can be ascertained. Comparison shows that cycloauration imposes much more acute angles at the chalcogenide atoms (P-E-Au) in the gold complexes. In complexes **17b** and **17c** the P-E-Au angles are 95.24(5) and 91.759(18)° compared with unconstrained angles of 102-116° and 97-111° for Ph_3PS and Ph_3PSe complexes respectively. The P-O-Au bond angle of the cycloaurated phosphine oxide complex **1** is 117.0(2)°.[7] In earlier work on *ortho*-manganated triphenylphosphine chalcogenides Depree *et al.* suggested that incorporation of $Ph_3P{=}O$ into a five-membered ring results in an unfavourable P-O-M bond angle at the oxygen.[9]

Compound **18** crystallised in the space group $Pna2_1$, with two unique molecules in the asymmetric unit; one of these molecules is depicted in Figure 3, clearly confirming the presence of the cycloaurated thiophosphorylic compound. Selected bond parameters are listed in Table 4. In both independent molecules the coordination around the gold atom is essentially square planar, with the largest deviations from the coordination plane of the metal being 0.0183(17) Å [C(2), molecule A] and 0.0181(11) Å [Au(1), molecule B]. As with **17b** and **17c**, the bite angle of the ligand is approximately 90°. The P-S-Au angles are 94.58(6)° (molecule 1) and 95.30(6)° (molecule 2) which are again severely acute and lead to the metallacyclic ring being extremely puckered. In both molecules it is the sulfur and phosphorus atoms that show the greatest deviation from the metallacyclic ring. The Au-S bond lengths are 2.3108(14) Å (molecule A) and 2.3064(13) Å (molecule B), which are comparable to the Au-S bond length in **17b** (2.3073(11) Å). As expected, the Au-Cl bonds

trans to the carbon [2.3700(13), 2.3715(12) Å] are longer than those *trans* to the sulfur [2.3178(13), 2.3205(13) Å]. Interestingly, substituting two phenyl groups (**17b**) for diethylamino groups (**18**) results in an increase in Au-Cl bond lengths. The Au-Cl bond *trans* to the sulfur in **17b** is 2.3094(12) Å – this increases to 2.3178(13) and 2.3205(13) Å in **18** indicating that the amine-substituted ligand has a greater *trans* influence than the phenyl substituted ligand.

Spectroscopic and mass spectrometric characterisation of cycloaurated phosphine chalcogenides

The presence of phosphorus in these compounds introduces a powerful (^{31}P) NMR spectroscopic probe which aids in both characterisation of the final products and in monitoring reactions. In isoelectronic iminophosphorane complexes there are small changes in chemical shift of the compounds upon *ortho*-mercuration followed by a larger predictable downfield shift of approximately 40 ppm after transmetallation to the gold,[33,34] attributed to the phosphorus entering a cyclic environment.[35] The trend is not as obvious in the present chalcogenide series, with only small unpredictable changes between the ligand, *ortho*-mercurated and cycloaurated complexes hence other effects must be contributing to the ^{31}P chemical shift. Table 5 presents the ^{31}P{^{1}H} NMR data for the complexes studied.

As discussed by Glidewell *et al.*,[36] the coordination of phosphine selenides to metal centres results in significant deshielding of the selenium nucleus and a decrease in the $^{1}J_{PSe}$ coupling constant – this is observed in the series of Ph_3P=Se complexes. There is only a small change (47 Hz) upon mercuration which indicates little interaction between the selenium and the mercury atom. Transmetallation to gold sees a decrease in the value of $^{1}J_{PSe}$ by 259 Hz which indicates a strong selenium – gold interaction. In addition, the value of $^{1}J_{PSe}$

is related to P-Se bond lengths in the solid state – the longer the P-Se bond the smaller $^1J_{PSe}$ is. This is in accordance with X-ray crystallographic data: the P-Se bond length in $Ph_3P{=}Se$ is 2.112(1) Å and $^1J_{PSe}$ is 731 Hz and in the cycloaurated complex the P-Se bond length is 2.1839(6) Å with $^1J_{PSe}$ = 425 Hz.

The P=E vibrations in $Ph_3P{=}S$ and $Ph_3P{=}Se$ occur at 638 cm^{-1} and 561 cm^{-1} respectively. Upon coordination to the metal this decreases to 603 cm^{-1} for **15** and further still to 597 cm^{-1} for **17b**. In the case of the selenide derivatives, the mercury compound **12c** shows no change in the P=Se vibration upon mercuration, however coordination to the gold (**17c**) gives a shift to 545 cm^{-1}. This further supports the inference from the NMR data that there is little interaction between the selenium and mercury. Likewise, $PhP(S)(NEt_2)_2$ has a P=S vibration at 604 cm^{-1} which moves to lower energy for the mercury complex **16** (597 cm^{-1}) and the cycloaurated species **18** (586 cm^{-1}). These decreases mirror those seen by King and McQuillan, and are attributed to a weakening of the P-E π bonds upon coordination to the metal.[37]

Reaction of $(2\text{-}AuCl_2C_6H_4)P(S)(NEt_2)_2$, 18 with thiosalicylic acid

Because gold(III) thiosalicylate derivatives often show a greater biological activity than the parent dichloride complex,[38,39,40,41] compound **18** was reacted with a molar equivalent of thiosalicylic acid and excess Me_3N in methanol to give the thiosalicylate complex **19** in good yield. In previous examples of gold(III) thiosalicylate complexes the ligand is coordinated so that the two soft σ donor ligands are mutually *cis* due to the *anti*-symbiotic effect.[42,43] Therefore, it is assumed that **19** is also the isomer where the carbon and the thiosalicylate sulfur are *cis* to each other.

Given the interest in biological activity of gold(III) complexes, with promising results,[44,45,46] some of the phosphine chalcogenide complexes reported herein have been subject to preliminary screening. Complex **19** shows modest activity (IC_{50} 1522 ng mL^{-1}) against the P388 murine leukemia cell line, while **17b** shows poor activity (IC_{50} >12500 ng mL^{-1}), and that of **18** is intermediate (3474 ng mL^{-1})

Conclusions

Three new *ortho*-metallated gold(III) complexes containing phosphine chalcogenide ligands have been synthesised by transmetallation from organomercury substrates and fully characterised. These are rare examples of cycloaurated complexes which contain a neutral donor ligand other than nitrogen. The complexes with the neutral sulfur donors appear to show similar qualitative stability to cycloaurated C,N complexes, which is interesting as they contain a oxidising gold(III) centre and a potentially reducing phosphine chalcogenide ligand. Reactivity also appears to be similar to the C,N auracycles: the *cis* chloride ligands can be replaced by the chelating dianionic thiosalicylate ligand to give a bi-metallacyclic complex which shows better biological activity than the parent complex against the P388 murine leukemia cell line.

Experimental

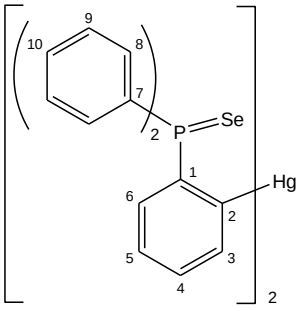
General

General experimental procedures were as described previously.[47] Compounds **11**, **12a**, **12b** and **3b** were prepared by literature procedures.[9,16] $Me_4N[AuCl_4]$ was prepared by addition of excess Me_4NCl to an aqueous solution of $H[AuCl_4]$. The reagents $HgCl_2$ (BDH), $PhP(NEt_2)_2$

(Aldrich), selenium powder (BDH), thiosalicylic acid (Sigma), tetramethyammonium chloride (Aldrich) and *n*-butyllithium (2.0 M in cyclohexane, Aldrich) were used as received.

Synthesis of 2-Hg($C_6H_4P(Se)Ph_2$)$_2$ 12c

2-Hg($C_6H_4PPh_2$)$_2$ **11** (0.300 g, 0.42 mmol) and grey selenium powder (0.066 g, 0.84 mmol) were added to dry degassed toluene (50 mL) and sonicated in an ultrasonic bath at 50 °C until the majority of the Se had disappeared (~16 h). The toluene was removed under vacuum and the white solid extracted into dichloromethane (3 × 10 mL). Petroleum spirits (30 mL) was added to the filtrate and storage at -20 °C gave 2-Hg($C_6H_4P(Se)Ph_2$)$_2$ **12c** as a white solid (0.225 g, 61%). Found: C 49.1, H 3.3, $C_{36}H_{28}P_2Se_2Hg$ requires C 49.1, H 3.2%. NMR: ^{1}H: δ 7.05 (m, 4H, H-5 and H-6), 7.40 (m, 2H, H-4), 7.42 (m, 8H, H-9), 7.47 (m, 4H, H-10), 7.68 (m, 8H, H-8), 7.78 (m, 2H, H-3); ^{13}C{^{1}H}: δ 125.6 (d, $^3J_{PC}$ 12.6 Hz, C-5), 128.6 (d, $^3J_{PC}$ 12.6 Hz, C-9), 130.3 (d, $^4J_{PC}$ 3.6 Hz, C-4), 131.6 (d, $^4J_{PC}$ 2.4 Hz, C-10), 132.3 (d, $^2J_{PC}$ 15.8 Hz, C-6), 132.4 (d, $^1J_{PC}$ 75.2 Hz, C-7), 133.2 (d, $^2J_{PC}$ 9.7 Hz, C-8), 140.2 (d, $^1J_{PC}$ 84.9 Hz, C-1), 140.8 (d, $^3J_{PC}$ 19.4 Hz, C-3), 175.4 (d, $^2J_{PC}$ 25.1 Hz, C-2); ^{31}P{^{1}H}: δ 41.4 ($^3J_{HgP}$ 284 Hz, $^1J_{SeP}$ 684 Hz) ppm. ESI-MS: *m/z*: 904.964 (100%, [M+Na]$^+$, calc 904.960), 841.040 (44%, [M-Se+O+Na]$^+$, calc 841.038), 819.064 (20%, [M-Se+O+H], calc 819.056), 882.981 (15%, [M+H]$^+$, calc 882.978); $AgNO_3$ added: 988.880 (100%, [M+Ag]$^+$, calc 988.876), 926.957 (25%, [M-Se+O+Ag]$^+$, calc 926.954). IR: υ(P=Se) 562 (m) cm^{-1}.



NMR numbering scheme for 2-Hg($C_6H_4P(Se)Ph_2$)$_2$ **12c**

Synthesis of (2-HgClC$_6$H$_4$)P(S)Ph$_2$ 15

(2-Mn(CO)$_4$C$_6$H$_4$)P(S)Ph$_2$ **3b** (0.406 g, 0.88 mmol) and HgCl$_2$ (0.477 g, 1.77 mmol) were refluxed in methanol (15 mL) for 3 h. The white solid that formed was removed by filtration and the filtrate reduced in volume to give a white solid. This was subsequently re-dissolved in the minimum dichloromethane and passed through a column of Celite. Removal of the dichloromethane gave (2-HgClC$_6$H$_4$)P(S)Ph$_2$ **15** as a white solid (0.339 g, 73%). Found: C 40.8, H 2.7; C$_{18}$H$_{14}$PSClHg requires C 40.8, H 2.7 %. NMR: ^{1}H: δ 7.30 (m, 1H, H-5), 7.39 (m, 1H, H-6), 7.47 (m, 4H, H-9), 7.55 (m, 3H, H-4 and H-10), 7.63 (m, 4H, H-8). 7.70 (m, 1H, H-3); ^{31}C{^{1}H}: δ 127.5 (d, $^3J_{PC}$ 11.8 Hz, C-5), 129.0 (d, $^3J_{PC}$ 12.7 Hz, C-9), 131.6 (d, $^4J_{PC}$ 3.5 Hz, C-4), 132.1 (d, $^1J_{PC}$ 86.3 Hz, C-7), 132.3 (d, $^4J_{PC}$ 3 Hz, C-10), 132.6 (d, $^2J_{PC}$ 10.6 Hz, C-8), 133.5 (d, $^2J_{PC}$ 13.8 Hz, C-6), 136.8 (d, $^1J_{PC}$ 89.0 Hz, C-1), 138.9 (d, $^3J_{PC}$ 17.1 Hz, C-3), 155.8 (d, $^2J_{PC}$ 19.8 Hz, C-2); ^{31}P{^{1}H}: δ 48.2 ($^3J_{HgP}$ 385 Hz) ppm. Scheme 3 gives the NMR numbering system. ESI-MS: *m/z*: 789.093 (100%, [2-Hg(C$_6$H$_4$P(S)Ph$_2$)$_2$+H]$^+$, calc 789.089), 1023.016 (20%, [2M-Cl]$^+$, calc 1023.018), 552.980 (9%, [M+Na]$^+$, calc 552.983). IR: υ(P=S) 603 (m) cm^{-1}.

Synthesis of (2-AuCl$_2$C$_6$H$_4$)P(S)Ph$_2$ 17b

2-Hg[(C$_6$H$_4$)P(S)Ph$_2$]$_2$ **12b** (0.100 g, 0.13 mmol), [Me$_4$N][AuCl$_4$] (0.105 g, 0.26 mmol) and [Me$_4$N]Cl (0.014 g, 0.13 mmol) were stirred overnight in degassed acetonitrile (15 mL) in a foil-covered flask. The acetonitrile was removed under vacuum and the residue extracted into dichloromethane (2 × 10 mL) and filtered. Slow addition of diethyl ether to the filtrate produced yellow crystals of (2-AuCl$_2$C$_6$H$_4$)P(S)Ph$_2$ **17b** (0.060 g, 42%). Found: C 38.4, H 2.6; C$_{18}$H$_{14}$PSCl$_2$Au requires C 38.5, H 2.5 %. NMR: ^{1}H: δ 6.97 (m, 1H, H-6), 7.30 (m, 1H, H-5), 7.45 (m, 1H, H-4), 7.64 (m, 4H, H-9), 7.72 (m, 2H, H-10), 7.76 (m, 4H, H-8), 8.46 (m, 1H, H-3); ^{13}C{^{1}H}: δ 125.0 (d, $^1J_{PC}$ 83.4 Hz, C-7), 127.9 (d, $^3J_{PC}$ 12.6 Hz, C-5), 130.2 (d, $^3J_{PC}$

13.7, C-9), 131.9 (d, $^{2}J_{PC}$ 14.3 Hz, C-6), 133.2 (d, $^{2}J_{PC}$ 11.5 Hz, C-8), 134.9 (d, $^{4}J_{PC}$ 3.3 Hz, C-4), 135.0 (d, $^{4}J_{PC}$ 2.7 Hz, C-10), 137.2 (d, $^{3}J_{PC}$ 14.8 Hz, C-3), 140.5 (d, $^{1}J_{PC}$ 100.0 Hz, C-1), 152.0 (d, $^{2}J_{PC}$ 16.1 Hz, C-2); $^{31}P\{^{1}H\}$: δ 56.4 ppm. Scheme 3 gives the NMR numbering system. ESI-MS: *m/z*: 578.999 (100%, $[M\text{-}Cl+OMe+Na]^{+}$, calc 578.998), 1081.002 (15%, $[2M\text{-}2Cl+OMe]^{+}$, calc 1080.999), 1135.010 (14%, $[2M\text{-}2Cl+2OMe+Na]^{+}$, calc 1135.008). IR: υ(P=S) 597 (m) cm^{-1}.

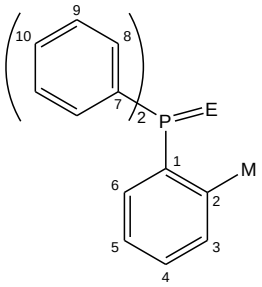
Alternative synthesis:

(2-$HgClC_6H_4$)P(S)Ph_2 **15** (0.250 g, 0.47 mmol), $[Me_4N][AuCl_4]$ (0.195 g, 0.47 mmol) and $[Me_4N]Cl$ (0.052 g, 0.47 mmol) were stirred in degassed acetonitrile (20 mL) for 24 h in a foil-covered flask. The acetonitrile was removed under vacuum and the residue extracted into dichloromethane (2 × 10 mL) and filtered. Slow addition of diethyl ether to the filtrate produced yellow crystals of (2-$AuCl_2C_6H_4$)P(S)Ph_2 **17b** (0.121 g, 46%), identified by NMR and ESI mass spectrometry.

Synthesis of (2-$AuCl_2C_6H_4$)P(Se)Ph_2 17c

2-$Hg[(C_6H_4)P(Se)Ph_2]_2$ **12c** (0.100 g, 0.11 mmol), $[Me_4N][AuCl_4]$ (0.094 g, 0.22 mmol) and $[Me_4N]Cl$ (0.012 g, 0.11 mmol) were stirred in degassed acetonitrile (10 mL) for 3 h in a foil covered flask. The solvent was removed under reduced pressure and the resulting yellow solid extracted into dichloromethane (2 × 10 mL) and filtered. The resulting filtrate was treated with diethyl ether (20 mL) and storage at -20 °C gave yellow crystals of (2-$AuCl_2C_6H_4$)P(Se)Ph_2 **17c** (0.082 g, 61%). NMR: ^{1}H: δ 6.87 (m, 1H, H-6), 7.29 (m, 1H, H-5), 7.45 (m, 1H, H-4), 7.64 (m, 4H, H-9), 7.71 (m, 2H, H-10), 7.75 (m, 4H, H-8), 8.51 (m, 1H, H-3); $^{13}C\{^{1}H\}$: δ 124.5 (d, $^{1}J_{PC}$ 75.4 Hz, C-7), 127.5 (d, $^{3}J_{PC}$ 13.0 Hz, C-5), 130.2 (d, $^{3}J_{PC}$ 13.4 Hz, C-9), 132.6 (d, $^{2}J_{PC}$ 13.9 Hz, C-6), 133.5 (d, $^{2}J_{PC}$ 11.9 Hz, C-8), 134.8 (d, $^{4}J_{PC}$

3.0 Hz, C-4), 134.9 (d, $^{4}J_{PC}$ 3.0 Hz, C-10), 138.5 (d, $^{3}J_{PC}$ 14.8 Hz, C-3), 140.9 (d, $^{1}J_{PC}$ 96.0 Hz, C-1), 150.2 (d, $^{2}J_{PC}$ 19.4 Hz, C-2); $^{31}P\{^{1}H\}$ δ 38.8 ($^{1}J_{SeP}$ 425 Hz) ppm. Scheme 3 gives the NMR labelling scheme. ESI-MS: *m/z*: 630.890 (100%, $[M+Na]^{+}$, calc 630.893), 1238.793 (28%, $[2M+Na]^{+}$, calc 1238.797), 1180.838 (9%, $[2M-Cl]^{+}$, calc 1180.838). IR: υ(P=Se) 562 (m) cm^{-1}.



Scheme 3 NMR numbering scheme for **15** (M = HgCl, E = S), **17b** (M = $AuCl_2$, E = S) and **17c** (M = $AuCl_2$, E = Se).

Synthesis of $PhP(S)(NEt_2)_2$

$PhP(NEt_2)_2$ (2 mL, 7.9 mmol) and sulfur (0.275 g, 8.6 mmol) were stirred under nitrogen overnight in dry degassed hexanes (50 mL). The solvent was removed under reduced pressure to give a pale yellow oil that failed to crystallise (1.40 g, 62%). Found: C 59.3, H 9.1, N 9.9; $C_{14}H_{25}N_2PS$ requires C 59.1, H 8.9, N 9.9%. NMR: ^{1}H: δ 1.04 (t, 12H, H-8), 3.13 (m, 8H, H-7), 7.42 (m, 3H, H-3, H-4 and H-5), 7.93 (m, 2H, H-2 and H-6); $^{13}C\{^{1}H\}$: δ 13.5 (d, $^{3}J_{PC}$ 4 Hz, C-8), 39.4 (d,$^{2}J_{PC}$ 4 Hz, C-7), 128.2 (d, $^{3}J_{PC}$ 14 Hz, C-3 and C-5), 130.9 (d, $^{4}J_{PC}$ 3 Hz, C-4), 131.7 (d, $^{2}J_{PC}$ 10 Hz, C-2 and C-6), 135.7 (d, $^{1}J_{PC}$ 123 Hz, C-1); $^{31}P\{^{1}H\}$: δ 78.4 ppm. Scheme 4 gives the NMR numbering scheme. ESI-MS: *m/z*: 307.138 (100%, $[M+Na]^{+}$, calc 307.137), 591.287 (5%, $[2M+Na]^{+}$, calc 591.284). IR: υ(P=S) 604 cm^{-1}.

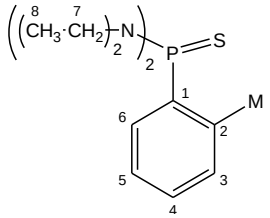
Synthesis of (2-HgClC$_6$H$_4$)P(S)(NEt$_2$)$_2$ 16

PhP(S)(NEt$_2$)$_2$ (0.500 g, 1.76 mmol) was dissolved in dry, degassed diethyl ether (20 mL). *n*-Butyllithium (0.9 mL, 1.76 mmol) was added dropwise to give a yellow solution that was stirred for 22 h. HgCl$_2$ (0.478 g, 1.76 mmol) in THF (5 mL) was added dropwise and the resulting grey solution stirred for a further 4 h. The grey solid that had formed was filtered and the filtrated evaporated under reduced pressure. The residue was redissolved in dichloromethane (20 mL) and refiltered. The solvent was reduced in volume (to ~ 5 mL) and hexanes were added until the solution went cloudy. Storage at -20 °C gave white crystals of (2-HgClC$_6$H$_4$)P(S)(NEt$_2$)$_2$ **16** (0.503 g, 55%). Found: C 32.6, H 4.6, N 5.3; C$_{14}$H$_{24}$N$_2$PSClHg requires C 32.4, H 4.7, N 5.4%. NMR: ^{1}H: δ 1.05 (t, 12H, H-8), 3.12 (m, 8H, H-7), 7.32 (m, 1H, H-5), 7.47 (m, 1H, H-4), 7.57 (m, 1H, H-3), 7.84 (m, 1H, H-6); ^{13}C{^{1}H}: δ 13.6 (d, $^3J_{PC}$ 3.1 Hz, C-8), 39.9 (d, $^2J_{PC}$ 3.6 Hz, C-7), 127.1 (d, $^3J_{PC}$ 11.4 Hz, C-5), 130.8 (d, $^2J_{PC}$ 9.3 Hz, C-6), 131.0 (d, $^4J_{PC}$ 3.4 Hz, C-4), 138.7 (d, $^3J_{PC}$ 20.5 Hz, C-3), 139.7 (d, $^1J_{PC}$ 132.1 Hz, C-1), 156.9 (d, $^2J_{PC}$ 22.8 Hz, C-2); ^{31}P{^{1}H}: δ 83.1 ($^3J_{HgP}$ 414 Hz) ppm. Scheme 4 gives the NMR labelling system. ESI-MS: *m/z*: 1003.188 (100%, [2M-Cl]$^+$, calc 1003.186), 769.266 (55%, [2-Hg(C$_6$H$_4$P(S)(NEt$_2$)$_2$)$_2$+H]$^+$, calc 769.258), 543.071 (24%, [M+Na]$^+$, calc 543.068). IR: υ(P=S) 597 (s) cm^{-1}.

Synthesis of (2-AuCl$_2$C$_6$H$_4$)P(S)(NEt$_2$)$_2$ 18

(2-HgClC$_6$H$_4$)P(S)(NEt$_2$)$_2$ **16** (0.150 g, 0.29 mmol), [Me$_4$N][AuCl$_4$] (0.119 g, 0.29 mmol) and [Me$_4$N]Cl (0.032 g, 0.29 mmol) were stirred overnight in a foil-covered flask of degassed acetonitrile (15 mL), under a nitrogen atmosphere. The acetonitrile was removed under reduced pressure and the residue extracted into dichloromethane (2 × 10 mL). Hexanes (20 mL) were added and the solution stored at -20 °C to give fluffy yellow crystals of (2-AuCl$_2$C$_6$H$_4$)P(S)(NEt$_2$)$_2$ **18** (0.106 g, 66%). Found: C 30.0, H 4.5, N 4.9;

$C_{14}H_{24}N_2PSCl_2Au$ requires 30.5, H 4.4, N 5.1%. NMR: ^1H: δ 1.20 (t, 12H, H-8), 3.25 (m, 8H, H-7), 7.11 (m, 1H, H-6), 7.30 (m, 1H, H-5), 7.40 (m, 1H, H-4), 8.39 (m, 1H, H-3); $^{13}C\{^1H\}$: δ 13.9 ($^3J_{PC}$ 2.5 Hz, C-8), 40.7 ($^2J_{PC}$ 4.7 Hz, C-7), 127.4 ($^3J_{PC}$ 13.1 Hz, C-5), 129.9 ($^2J_{PC}$ 11.5 Hz, C-6), 134.7 ($^4J_{PC}$ 2.9 Hz, C-4), 135.8 ($^1J_{PC}$ 139.0 Hz, C-1), 136.2 ($^3J_{PC}$ 17.3 Hz, C-3), 144.0 ($^2J_{PC}$ 24.6 Hz, C-2); $^{31}P\{^1H\}$: δ 79.4 ppm. Scheme 4 gives the NMR labelling system. ESI-MS: *m/z*: 1067.114 (100%, $[2M-Cl]^+$, calc 1067.116), 573.033 (95%, $[M+Na]^+$, calc 573.033), 1061.166 (73%, $[2M-2Cl+OMe]^+$, 1061.168), 1125.072 (58%, $[2M+Na]^+$, calc 1125.075), 515.074 (38%, $[M-Cl]^+$, calc 515.075). IR: υ(P=S) 586 (m) cm^{-1}.

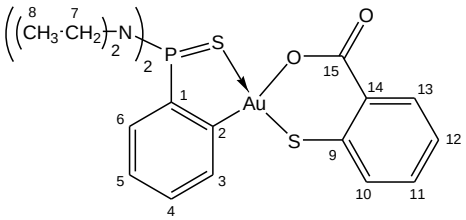


Scheme 4 NMR numbering scheme for $(Et_2N)_2P(S)Ph$ (M=H), **16** (M=HgCl) and **18** ($M=AuCl_2$).

Reaction of $(2\text{-}AuCl_2C_6H_4)P(S)(NEt_2)_2$ 18 with thiosalicylic acid

$(2\text{-}AuCl_2C_6H_4)P(S)(NEt_2)_2$ **18** (0.051 g, 0.09 mmol) and thiosalicylic acid (0.014 g, 0.09 mmol) were stirred in methanol (10 mL). To the dark orange solution Me_3N (1 mL, excess) was added resulting in the solution becoming immediately lighter. The solution was stirred for 90 min. in a foil covered flask before water (50 mL) was added to produce a fine precipitate. Stirring was continued for a further 12 h, the solution was filtered and the yellow solid washed with water (2 × 10 mL) and diethyl ether (1 × 10 mL). Drying under vacuum gave 0.043 g (76%) of the thiosalicylate derivative **19**. Found: C 39.9, H 4.5, N 4.5, $C_{21}H_{28}N_2O_2PS_2Au$ requires C 39.9, H 4.5, N 4.4%. NMR: ^1H: δ 1.14 (t, 12H, H-8), 3.25 (m,

8H, H-7), 7.12 (m, 1H, H-6), 7.18 (m, 2H, H-11 and H-12), 7.27 (m, 1H, H-5), 7.39 (m, 2H, H-4 and H-10), 7.93 (m, 1H, H-3), 8.16 (m, 1H, H-13); $^{13}C\{^{1}H\}$: δ 13.7 ($^{3}J_{PC}$ 2.8 Hz, C-8), 40.4 ($^{2}J_{PC}$ 4.5 Hz, C-7), 125.4 (C-12), 127.0 ($^{3}J_{PC}$ 13.0 Hz, C-5), 129.9 (C-10 and C-11), 130.4 ($^{2}J_{PC}$ 10.8 Hz, C-6), 133.2 (C-13), 134.0 ($^{4}J_{PC}$ 3.3 Hz, C-4), 134.1 (C-14), 134.2 ($^{3}J_{PC}$ 16.1 Hz, C-3), 134.7 ($^{2}J_{PC}$ 21.5 Hz, C-2), 136.8 (C-9), 141.6 ($^{1}J_{PC}$ 138.0 Hz, C-1), 168.6 (C-15); $^{31}P\{^{1}H\}$: δ 75.0 ppm. ESI-MS: *m/z*: 633.109 (100%, $[M+H]^{+}$, calc 633.107), 655.092 (64%, $[M+Na]^{+}$, calc 655.089), 763.254 (27%, $[2\text{-}Au(C_6H_4P(S)(NEt_2)_2)_2]^{+}$, calc 763.247), 1287.192 (21%, $[2M+Na]^{+}$, calc 1287.188), 1265.210 (6%, $[2M+H]^{+}$, calc 1265.206). IR: υ(P=S) 587 (m); υ(C=O) 1624 (vs) cm^{-1}.



NMR numbering scheme for **19**

Antitumour assays

Assays to determine the *in vitro* anti-tumour activity against the P388 Murine Leukemia cell line were carried out by Gill Ellis of the Marine Chemistry Group at the University of Canterbury. The sample was dissolved in the solvent and incubated with P388 murine leukemia cells for 72 h. IC_{50} values were determined using absorbance values obtained when the dye MMT tetrazolium (yellow) was reduced to MMT formazan (purple).

X-ray crystal structure determinations of 15, 17b, 17c and 18

In all cases single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane solution of the compound at room

temperature. Unit cell and intensity data were collected at the University of Auckland on a Bruker Smart CCD Diffractometer, operating at 89 K; crystallographic details are presented in Table 6. Absorption corrections were applied by semi-empirical methods (SADABS[48]).

The structures of **15** and **18** were solved by the direct methods option of SHELXS-97, **17b** and **17c** by the Patterson methods option.[49] In all cases the heavy metal was initially located and all other non-hydrogen atoms by a series of difference maps. Hydrogen atoms were placed in calculated positions. Refinement was with SHELXL-97.[50]

An initial inspection of **18** indicated that the two independent molecules in $Pna2_1$ were possibly related by an inversion centre. A closer examination showed that the heavy atoms (Au, P, N, S and Cl) were related by approximate symmetry but the lighter atoms were not. Attempts to solve and refine the structure in the centrosymmetric space group *Pnma* were not successful, confirming $Pna2_1$. Refinement suggested racemic twinning with 0.76:0.24 occupancy so this was included in the final model.

Supplementary material

Crystallographic data (excluding structure factors) for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. (743531) **15**, (743530) **17b,** (743528) **17c** and (743529) **18**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank The University of Waikato for financial support of this work, including technical support from Wendy Jackson and Pat Gread, and Prof. Alistair Wilkins for

assistance with NMR spectroscopy. KJK thanks The Tertiary Education Commission (Top Achievers Doctoral Scholarship) and the New Zealand Federation of Graduate Women (Merit Award for Doctoral Study). Dr. Tania Groutso (University of Auckland) is thanked for collection of the X-ray data sets, and Gill Ellis (University of Canterbury) for biological assay data.

Table 1 Selected structural parameters for the complex (2-$HgClC_6H_4$)$P(S)Ph_2$ **15**

Atoms	Lengths (Å)	Atoms	Angles (°)
P(1) – S(1)	1.9745(11)	S(1) – P(1) – C(11)	114.51(11)
P(1) – C(11)	1.824(3)	P(1) - C(11) – C(12)	121.3(2)
C(11) – C(12)	1.400(4)	C(11) – C(12) – Hg(1)	121.7(2)
C(12) – Hg(1)	2.068(3)	C(12) – Hg(1) – Cl(1)	173.34(9)
Hg(1) – Cl(1)	2.3273(8)	C(11) – P(1) – C(31)	106.25(14)
S(1)---Hg(1)	2.9585(8)	C(21) – P(1) – C(11)	105.86(14)

Table 2 Selected structural parameters for the complexes **17b** and **17c**

	17b (E=S)	**17c** (E=Se)
Bond lengths (Å)		
Au(1) – Cl(1)	2.3635(11)	2.3628(6)
Au(1) – Cl(2)	2.3094(12)	2.3222(6)
C(12) – Au(1)	2.045(5)	2.049(2)
E(1) – Au(1)	2.3073(11)	2.4091(3)
P(1) – E(1)	2.0324(16)	2.1839(6)
P(1) – C(11)	1.794(4)	1.783(2)
C(11) – C(12)	1.401(6)	1.406(3)
Bond angles (°)		
Cl(1) – Au(1) – Cl(2)	90.64(4)	90.52(2)
Cl(1) – Au(1) – E(1)	86.25(4)	84.876(18)
E(1) – Au(1) – C(12)	90.02(13)	91.16(7)
C(12) – Au(1) – Cl(2)	93.23(13)	93.60(7)
Au(1) – E(1) – P(1)	95.24(5)	91.759(18)
E(1) – P(1) – C(11)	104.57(15)	104.17(8)
C(11) – C(12) – Au(1)	120.2(3)	120.99(18)

Table 3 Results of a search of the Cambridge Crystallographic Database¶ for η^1 coordinated $Ph_3P{=}E$ ligands

	$Ph_3P{=}O$	$Ph_3P{=}S$	$Ph_3P{=}Se$
Sample number	357	19	11
Independent $XPPh_3$ moieties	636	24	13
Mean P-E-M angle (°)	158.2	109.1	104.0
Std deviation in P-E-M angle (°)	5.7	3.0	4.5
Range P-E-M angle (°)	125-180	102-116	97-111
P-E-Au angle (°)	*	95.24 (**17b**)	91.759 (**17c**)

¶ Version 5.30, May 2009 release. Only those hits with $R_1 \leq 0.075$ were included

* P-O-Au angle 117.0(2)° in complex **1**

Table 4 Selected structural parameters for the complex (2-$AuCl_2C_6H_4$)P(S)$(NEt_2)_2$ **18**

	Molecule A	Molecule B
Bond lengths (Å)		
Au(1) – Cl(1)	2.3700(13)	2.3715(12)
Au(1) – Cl(2)	2.3178(13)	2.3205(13)
Au(1) – S(1)	2.3108(14)	2.3064(13)
Au(1) – C(2)	2.059(5)	2.051(5)
P(1) – S(1)	2.0403(19)	2.0451(18)
P(1) – C(1)	1.781(5)	1.776(5)
C(1) – C(2)	1.398(7)	1.414(7)
P(1) – N(1)	1.628(5)	1.638(5)
P(1) – N(2)	1.623(4)	1.619(4)
Bond angles (°)		
Cl(1) – Au(1) – Cl(2)	91.49(5)	90.28(5)
Cl(2) – Au(1) – C(2)	93.21(15)	92.90(15)
Cl(1) – Au(1) – S(1)	85.88(5)	86.43(5)
C(2) – Au(1) – S(1)	89.42(14)	90.37(15)
Au(1) – S(1) – P(1)	94.58(6)	95.30(6)
S(1) – P(1) – C(1)	102.91(17)	102.68(17)
P(1) – C(1) – C(2)	116.2(4)	117.1(4)
C(1) – C(2) – Au(1)	119.3(4)	118.6(4)

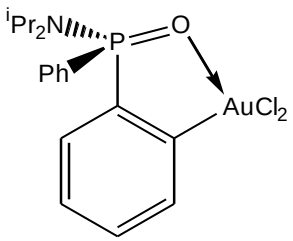
Table 5 $^{31}P\{^{1}H\}$ NMR chemical shifts (ppm) of the metallated phosphine chalcogenide ligands used in this study ($CDCl_3$)

	Ligand	***Ortho*-mercurated complex**	**Cycloaurated complex**
$Ph_3P=S$	44.0	48.2 ($^{3}J_{P\text{-}Hg}$ = 385 Hz)	56.4
$Ph_3P=Se$	36.0 ($^{1}J_{P\text{-}Se}$ = 731 Hz)	41.4 ($^{1}J_{P\text{-}Se}$ = 684 Hz) ($^{3}J_{P\text{-}Hg}$ = 284 Hz)	38.8 ($^{1}J_{P\text{-}Se}$ = 425 Hz)
$PhP(S)(NEt_2)_2$	78.4	83.1 ($^{3}J_{P\text{-}Hg}$ = 414 Hz)	79.4

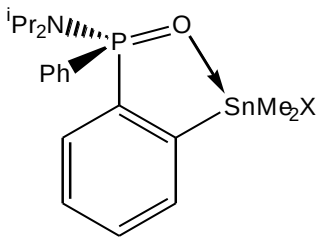
Table 6 Crystal and refinement data for the complexes **15**, **17b**, **17c** and **18**

Complex	**15**	**17b**	**17c**	**18**
Formula	$C_{18}H_{14}PSClHg$	$C_{18}H_{14}PSCl_2Au$	$C_{18}H_{14}PCl_2SeAu$	$C_{14}H_{24}N_2PSCl_2Au$
Molecular mass	529.36	561.19	608.09	551.25
T/K	89	89	89	89
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	P-1	P-1	$Pna2_1$
a (Å)	8.8845(1)	8.1875(1)	8.1506(1)	27.3998(9)
b (Å)	17.2034(1)	9.1443(1)	9.2374(1)	7.9520(3)
c (Å)	11.2712(2)	12.4011(1)	12.4369(2)	17.1925(6)
α (°)	90	98.705(1)	80.142(1)	90
β (°)	101.8490(1)	102.795(1)	76.934(1)	90
γ (°)	90	90.484(1)	89.994(1)	90
V ($Å^3$)	1686.02(4)	894.124(16)	897.94(2)	3746.0(2)
Z	4	2	2	8
D_{calc} (g cm^{-3})	2.085	2.084	2.249	1.955
$T_{max,min}$	0.2524, 0.1026	0.2742, 0.2285	0.4170, 0.1553	0.2397, 0.2038
Number of unique reflections	3430	3657	4284	7379
Number of observed reflections [I>2σ(I)]	3258	3562	4147	6979
R[I>2σ(I)]	0.0200	0.0274	0.0152	0.0216
wR_2 (all data)	0.0525	0.0717	0.0360	0.0457
Goodness of Fit	1.060	1.106	1.073	1.130
Flack x parameter				0.2364(4)*

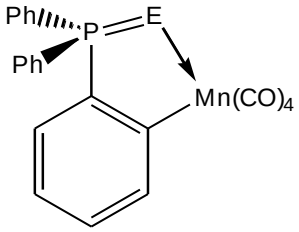
* Racemic twin (occupancy 0.76/0.24)



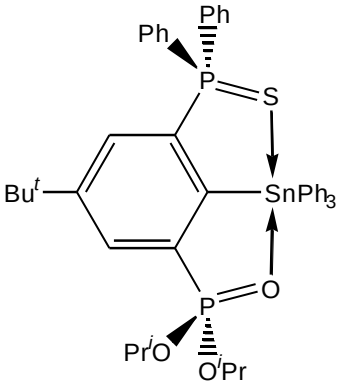
1



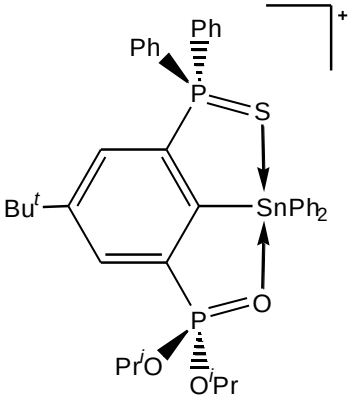
2, X = Cl or Me



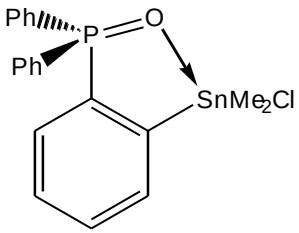
3a E=O
3b E=S
3c E=Se



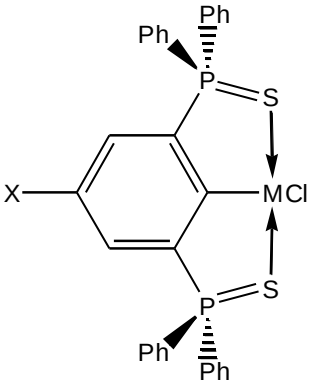
4



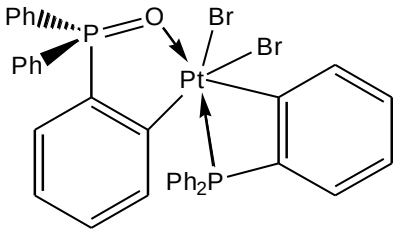
5



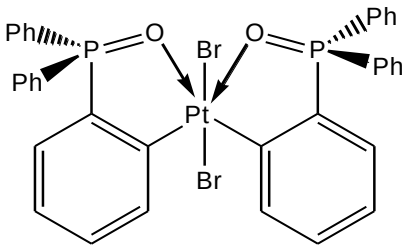
6



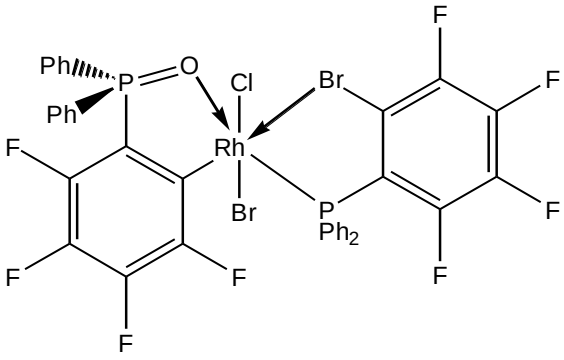
7a M=Pd, X=Me
7b M=Pt, X=Me
7c M=Pd, X=H



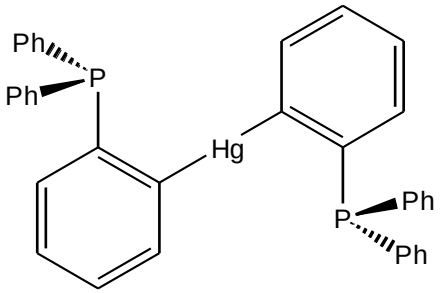
8



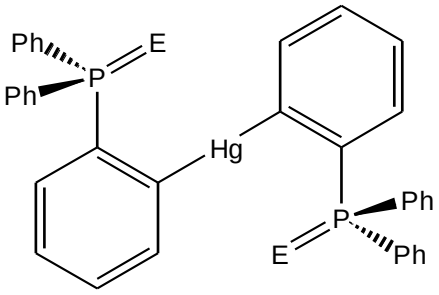
9



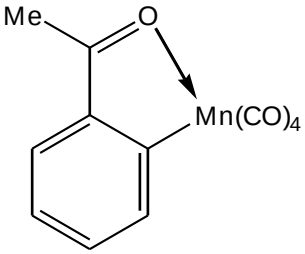
10



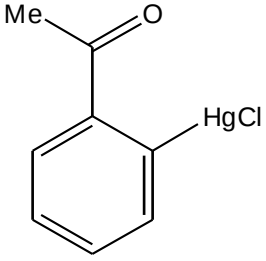
11



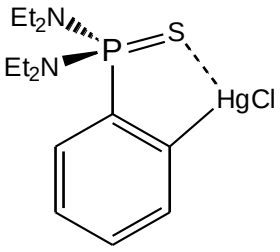
12a, E = O
12b, E = S
12c, E = Se



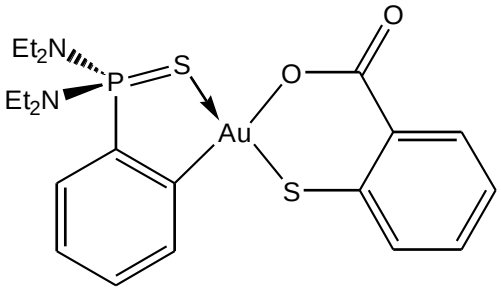
13



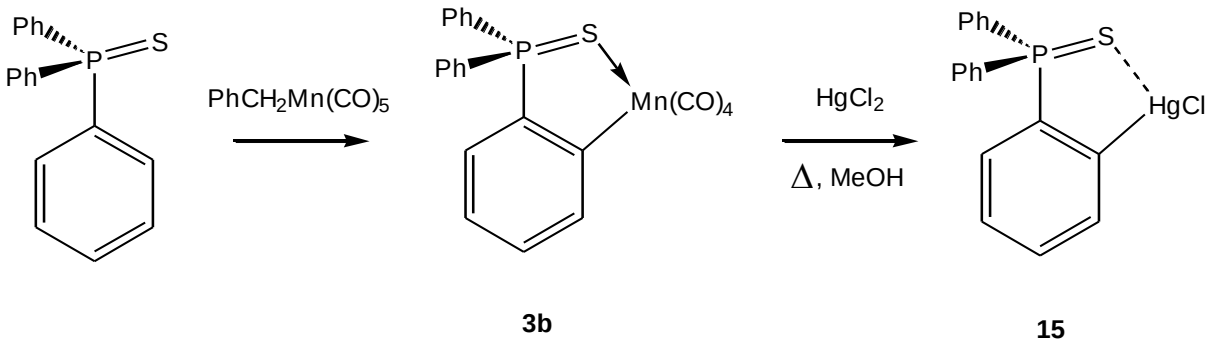
14



16

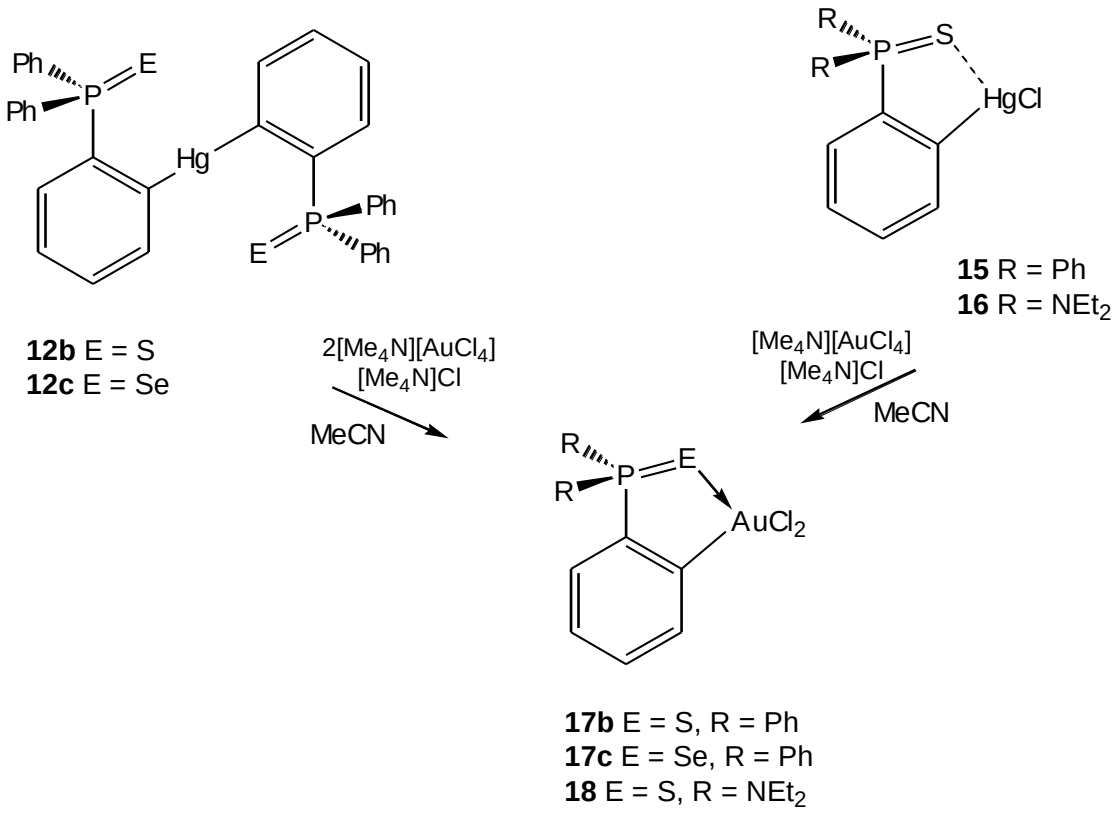


19



3b **15**

Scheme 1



12b E = S
12c E = Se

15 R = Ph
16 R = NEt_2

17b E = S, R = Ph
17c E = Se, R = Ph
18 E = S, R = NEt_2

Scheme 2

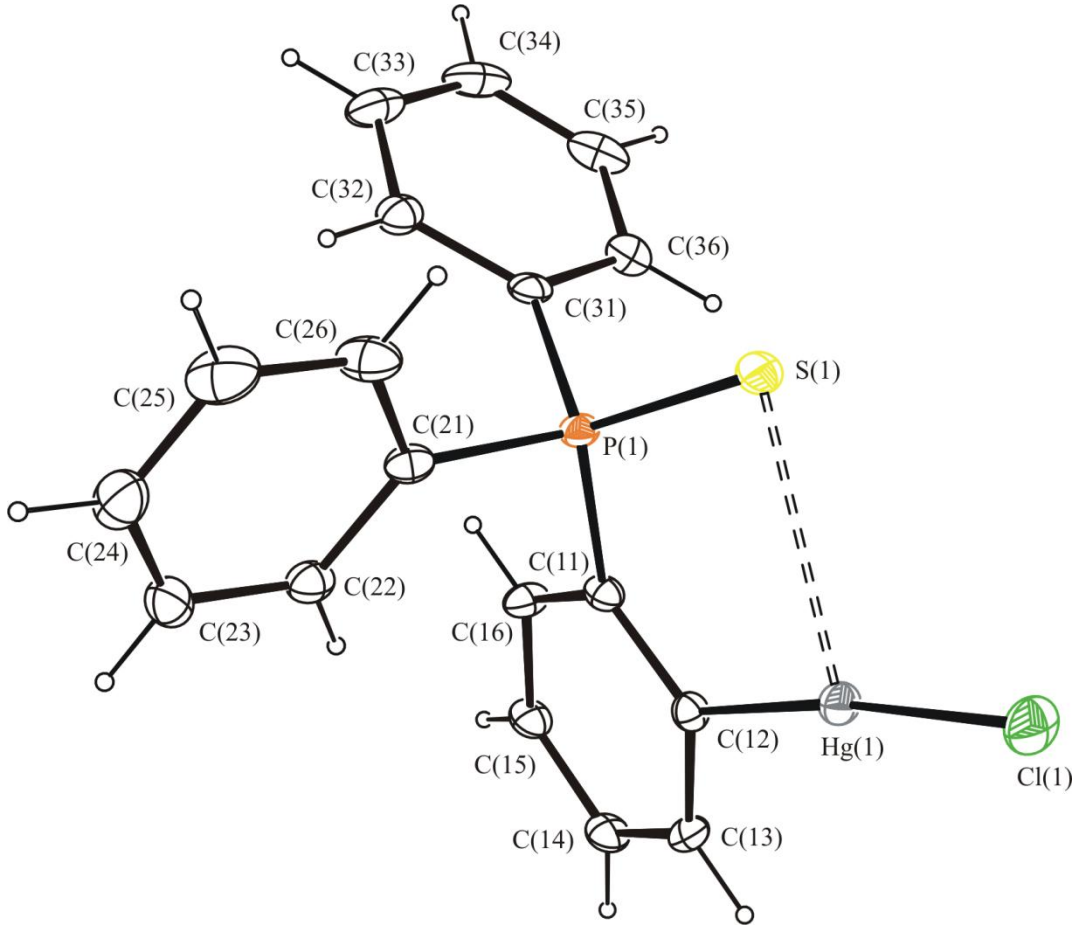


Figure 1 Structure of the complex (2-$HgClC_6H_4$)$P(S)Ph_2$ **15** showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

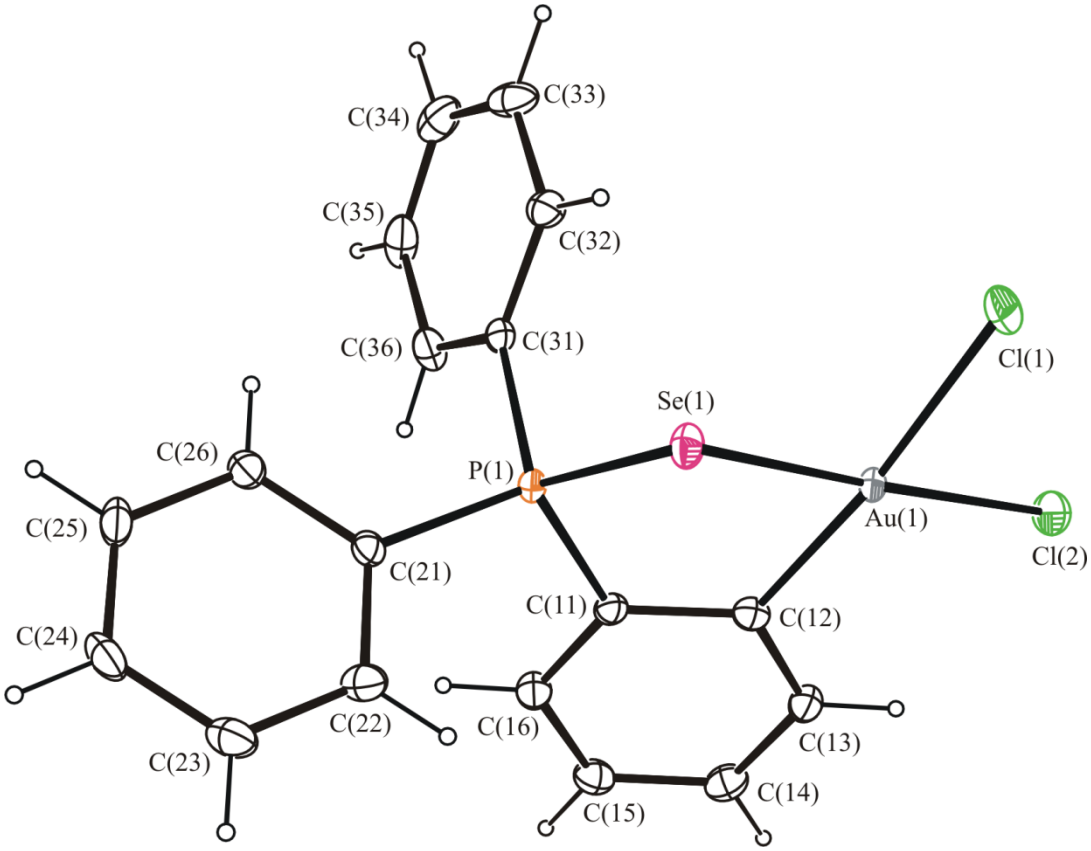


Figure 2 Molecular diagram of (2-$AuCl_2C_6H_4$)P(Se)Ph_2 **17c** indicating the atom numbering scheme, with thermal ellipsoids at the 50% probability level. The cycloaurated phosphine sulfide **17b** is isostructural, and has a comparable numbering scheme.

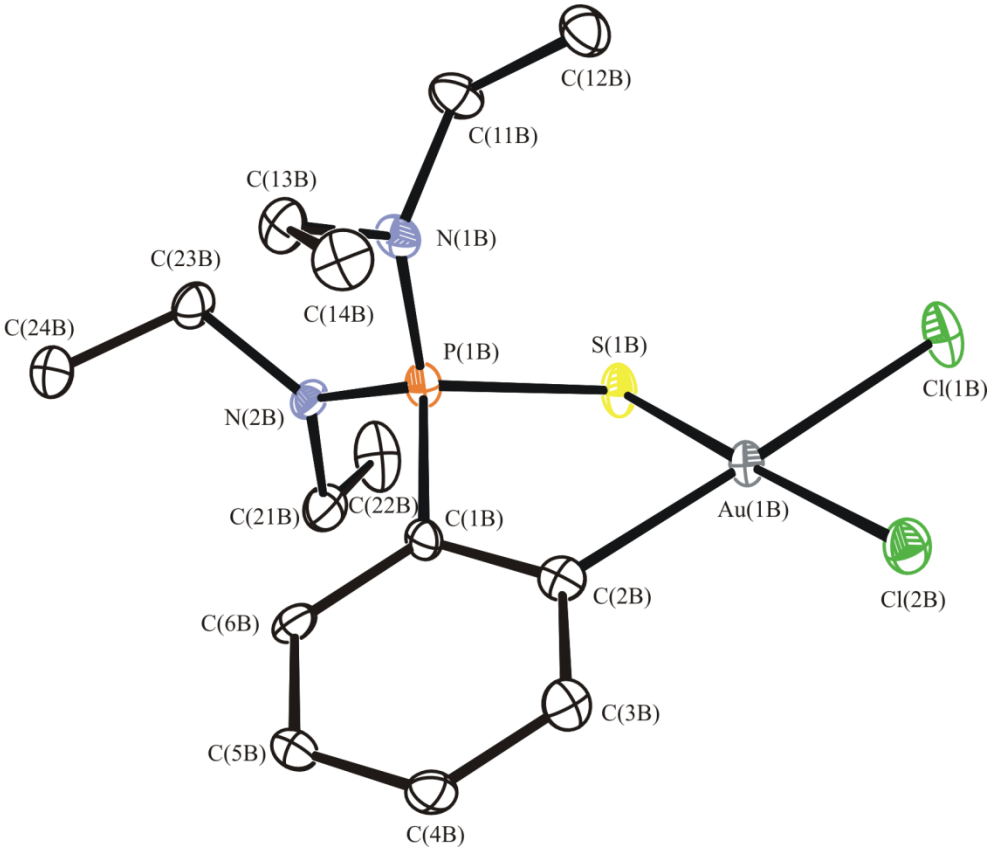


Figure 3 Molecular structure of (2-$AuCl_2C_6H_4$)P(S)(NEt_2)$_2$ **18** showing one of the unique molecules in the asymmetric unit. Hydrogen atoms have been excluded for clarity and thermal ellipsoids are shown at the 50% probability level.

References

[1] T. S. Lobana, *Prog. Inorg. Chem*., 1989, **37**, 495.

[2] T. S. Lobana, *Coordination Chemistry of Phosphine Chalcogenides and Their Analytical and Catalytic Applications in: The Chemistry of Organophosphorus Compounds*, Vol 2, John Wiley and Sons Ltd, 1992, Chapter 8, page 409.

[3] R. Usón, A. Laguna and J. L. Sanjoaquin, *J. Organomet. Chem*., 1974, **80**, 147.

[4] R. Usón, A. Laguna, M. Laguna, J. Jiménez and M. E. Durana, *Inorg. Chim. Acta,* 1990, **168**, 89.

[5] A. Laguna, M. Laguna, J. Jiménez and A. J. Fumanal, *J. Organomet. Chem*., 1990, **396**, 121.

[6] M. Contel, A. J. Edwards, J. Garrido, M. B. Hursthouse, M. Laguna and R. Terroba, *J. Organomet. Chem.*, 2000, **607**, 129.

[7] P. Oña-Burgos, I. Fernández, L. Roces, L. T. Fernández, S. García-Granda and F. López-Ortiz, *Organometallics*, 2009, **28**, 1739.

[8] W. Henderson, *Adv. Organomet. Chem.*, 2006, **54**, 207.

[9] G. J. Depree, N. D. Childerhouse and B. K. Nicholson, *J. Organomet. Chem.*, 1997, **533**, 143.

[10] J. Fischer, M. Schürmann, M. Mehring, U. Zachwieja and K. Jurkschat, *Organometallics*, 2006, **25**, 2886.

[11] H. Hartung, D. Petrick, C. Schmoll and H. Weichmann, *Z. Anorg. Allg. Chem*., 1987, **550**, 140.

[12] T. Kanbara and T. Yamamoto, *J. Organomet. Chem.*, 2003, **688**, 15.

[13] M. A. Bennett, S. K. Bhargava, M. Ke and A. C. Willis, *J. Chem. Soc., Dalton Trans*., 2000, 3537.

[14] X. Solans, M. Font-Altaba, M. Aguilo, C. Miravitlles, J. C. Besteiro and P. Lahuerta, *Acta Cryst. Sect. C*, 1985, **41**, 841.

[15] M. A. Bennett, M. Contel, D. C. R. Hockless and L. L. Welling, *Chem. Commun*., 1998, 2401.

[16] M. A. Bennett, M. Contel, D. C. R. Hockless, L. L. Welling and A. C. Willis, *Inorg.* Chem., 2002, **41**, 844.

[17] R. C. Larock, *Organomercury Compounds in Synthesis*, Springer-Verlag, Berlin, 1985.

[18] F. Montilla, A. Galindo, V. Rosa and T. Avilés, *Dalton Trans*., 2004, 2588.

[19] W. Henderson, B. K. Nicholson and L. J. McCaffrey, *Polyhedron*, 1998, **17**, 4291.

[20] W. Henderson and G. M. Olsen, *Polyhedron*, 1998, **17**, 577.

[21] W. Henderson and G. M. Olsen, *Polyhedron*, 1996, **15**, 2105.

[22] L. Main and B. K. Nicholson, *Adv. Metal-Org. Chem*., 1994, **3**, 1.

[23] J. M. Cooney, L. H. P. Gommans, L. Main and B. K. Nicholson, *J. Organomet. Chem.*, 1987, **336**, 293.

[24] T. S. Lobana, M. K. Sandhu, M. J. Liddell and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1990, 691.

[25] T. S. Lobana, R. Verma, A. Singh, M. Shikha and A. Castiñeiras, *Polyhedron*, 2002, **21**, 205.

[26] P. W. Codding and K. A. Kerr, *Acta Cryst. Sect. B*, 1978, **34**, 3785.

[27] D. C. Craig, N. K. Roberts and J. L. Tanswell, Aust. J. Chem., 1990, **43**, 1487.

[28] P. G. Jones, C. Kienitz and C. Thoene, *Z. Kristallogr*., 1994, **209**, 80.

[29] M. C. Gimeno, P. G. Jones, A. Laguna and C. Sarroca, *J. Organomet. Chem*., 2000, **596**, 10.

[30] H. H. Murray, G. Garzón, R. G. Raptis, A. M. Mazany, L. C. Porter and J. P. Fackler Jnr., *Inorg. Chem.*, 1988, **27**, 836.

[31] S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Z. Naturf.*, 2007, **62b**, 407.

[32] CCDC; Version 5.30, May 2009 release. For a more detailed analysis see J. B. Cook, B. K. Nicholson and D. W. Smith, *J. Organomet. Chem.*, 2004, **689**, 860.

[33] S. D. J. Brown, W. Henderson, K. J. Kilpin and B. K. Nicholson, *Inorg. Chim. Acta*, 2007, **360**, 1310.

[34] K. J. Kilpin, W. Henderson and B. K. Nicholson, *Inorg. Chim. Acta*, 2009, **362**, 3669.

[35] P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

[36] C. Glidewell and E. J. Leslie, *J. Chem. Soc., Dalton Trans*., 1977, 527.

[37] M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 1967, 898.

[38] K. J. Kilpin, W. Henderson and B. K. Nicholson, *Polyhedron*, 2007, **26**, 434.

[39] M. B. Dinger and W. Henderson, *J. Organomet. Chem.*, 1998, **560**, 233.

[40] W. Henderson, B. K. Nicholson, S. J. Faville, D. Fan and J. D. Ranford, *J. Organomet. Chem.*, 2001, **631**, 41.

[41] D. Fan, C.-T. Yang, J. D. Ranford, J. J. Vittal and P. F. Lee, *Dalton Trans*., 2003, 3376.

[42] T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.

[43] R. G. Pearson, *Inorg. Chem*., 1973, **12**, 712.

[44] E. R. T. Tiekink, *Critical Rev. Onc./Hem.*, 2002, **42**, 225.

[45] R. V. Parish, *Met.-Based Drugs*, 1999, **6**, 271.

[46] C. Gabbiani, A. Casini and L. Messori, *Gold Bull.*, 2007, **40**, 73.

[47] K. J. Kilpin, W. Henderson and B. K. Nicholson, *Dalton Trans*., 2008, 3899.

[48] R. H. Blessing, *Acta Cryst. Sect. A*, 1995, **51**, 33.

[49] G. M. Sheldrick, SHELXS-97 - A Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.

[50] G. M. Sheldrick, SHELXL-97 - A Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.