Phenylene-1,4- and biphenylene-4,4'-diselenolate bridged complexes of gold(I)¹

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Abstract: Homobimetallic gold-selenolate complexes of the type $[(Ph_2R)PAuSe(C_6H_4)_nSeAuP(Ph_2R)]$ (3a, R = Et, n = 1; 3b, R = Et, n = 2; 5a, R = Ph, n = 1; 5b, R = Ph, n = 2) are obtained by the reaction of $[Ph_2RPAuCl]$ (1, R = Et; 4, R = Ph) with 0.5 equiv. of Me₃SiSe(C₆H₄)_nSeSiMe₃ (2a, n = 1; 2b, n = 2) in good yield. Complex $[(Pr_3P)AuSe(C_6H_4)_2SeAu(PPr_3)]$ 7b can be prepared in a two-step synthesis procedure: treatment of $[AuCl(SMe_2)]$ 6 with 0.5 equiv. of Me₃SiSe(C₆H₄)₂SeSiMe₃ 2b gives $[(Me_2S)AuSe(C_6H_4)_2SeAu(SMe_2)]$, which further reacts with PPr₃ to afford 7b. The new gold-selenolate complexes have been characterized by multinuclear NMR (¹H, ³¹P, ⁷⁷Se) and elemental analysis. The solid state structures of 3b, 5a, and 7b were determined by single X-ray structure analysis.

Key words: gold, dimer, selenolate, biphenylene, phenylene.

Résumé : La réaction des produits de formule générale [Ph₂RPAuCl] (1, R = Et; 4, R = Ph) avec 0,5 équivalents de Me₃SiSe(C₆H₄)_nSeSiMe₃ (2a, n = 1; 2b, n = 2) conduit à la formation de complexes homobimétalliques sélénolate d'or du type [(Ph₂R)PAuSe(C₆H₄)_nSeAuP(Ph₂R)] (3a, R = Et, n = 1; 3b, R = Et, n = 2; 5a, R = Ph, n = 1; 5b, R = Ph, n = 2) avec de bons rendements. On peut préparer le complexe [(Pr₃P)AuSe(C₆H₄)₂Au(PPr₃)] (7b) par une méthode de synthèse en deux étapes dans laquelle le traitement du [AuCl(SMe₂)] (6) avec 0,5 équivalents de Me₃SiSe(C₆H₄)₂Se-SiMe₃ (2b) conduit à la formation du [(Me₂S)AuSe(C₆H₄)₂SeAu(SMe₂)] qui, par réaction subséquente avec du PPr₃, fournit le produit 7b. Les nouveaux complexes sélénolates d'or ont été caractérisés par la RMN multinucléaire (¹H, ³¹P et ⁷⁷Se) et par analyse élémentaire. Faisant appel à la diffraction des rayons X, on a déterminé les structures des produits 3b, 5a et 7b à l'état solide.

Mots-clés : or, dimère, sélénolate, biphénylène, phénylène.

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Introduction

The coordination chemistry of Au(I) is a most important branch of inorganic chemistry (1), and in particular there has been considerable interest in the study of gold(I) phosphine complexes of the type R_3 PAuL (L = anionic ligand) in part because of the successful use of auranofin (a second-line, orally administered gold drug) for the treatment of rheumatoid arthritis (2, 3). Recent reviews by McKeage et al. (4) and Tiekink (5) also highlight that Et₃PAuCl and other gold(I) phosphine complexes can act as potential anti-tumor agents. With the rapid explosion of the ligand chemistry of the heavier chalcogen elements, it is somewhat surprising that the chemistry of gold selenolates has been the focus of less attention, despite the great possibilities that the compounds can offer regarding their structures (6). Gold(I) selenolates, including mononuclear gold(I) complexes of the type $[Au(SeR)(PR_3)]$ (7, 8), have been prepared by the reaction of gold(I) chloride with selenols (9), or alkali metal selenolate salts (10, 11, 12), the coupling of stannyl diselenolate (13), the reaction with PhSeSiMe₃ (14, 15), as well as reactions between gold(I) chloride with organic selenolate ligands in the presence of $AgSbF_6$ (15). They have also been prepared by the reaction $Ph_3PAuN(SiMe_3)_2$ with selenols (16).

As part of our continued interest in developing the structural chemistry of metal-selenium interactions with conjugated diselenolate ligands (17), we report here a simple and efficient method for the synthesis and characterization of a small series of dimeric gold(I) selenolate complexes incorporating phosphines as ligands. These represent the first structures for gold selenolates of this type.

Results and discussion

When RPh_2PAuCl (1, R = Et; 4, R = Ph) was reacted with 0.5 equimolar amounts of 1,4-bis(trimethylsilylseleno)-phenylene (2a) or biphenylene-4,4'-bis(trimethylsilylselenium)

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Dedicated with thanks and admiration to Richard J. Puddephatt: a more magnanimous colleague will never be found.

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¹This article is part of a Special Issue dedicated to Professor R. Puddephatt. ²Corresponding author (e-mail: corrigan@uwo.ca). ³Deceased. Scheme 1.



Table 1. Selected NMR spectroscopic data for 3a, 3b, 5a, and 5b in CDCl₃ and yield.

Compound	³¹ P	⁷⁷ Se	Yield (%)
3a	38.9	148.6	72
3b	41.4	157.0	75
5a	39.9	148.2	71
5b	39.6	156.6	73
7b	32.5	143.7	75

Note: Chemical shifts are reported in ppm.

(2b), the digold(I) selenolate complexes [(RPh_2P)AuSe-(C_6H_4)_nSeAu(PPh_2R)] (3a, R = Et, n = 1; 3b, R = Et, n = 2; 5a, R = Ph, n = 1; 5b, R = Ph, n = 2) are formed, with the elimination of Me₃SiCl (Scheme 1). After appropriate work-up, 3a, 3b, 5a, and 5b can be isolated in yields between 71% and 75% as pale yellow solids.

Air stable **3a**, **3b**, **5a**, and **5b** are soluble in common organic solvents, including dichloromethane and chloroform. They were characterized by ¹H, ³¹P{¹H}, and ⁷⁷Se{¹H} NMR spectroscopy. The results are summarized in Table 1.

The ¹H NMR spectrum of [(EtPh₂P)AuSeC₆H₄SeAu(PPh₂Et)] 3a displays, in addition to the aromatic and aliphatic resonances from the phosphine ligands, a singlet for the aryl protons of the 1,4-phenylene moiety at 7.41 ppm. The ${}^{31}P{}^{1}H{}$ NMR spectra of solutions of 3a display one singlet for the two equivalent phosphorus atoms at 38.9 ppm with no evidence for satellites arising from ${}^{2}J_{PSe}$ coupling. The ⁷⁷Se{¹H} NMR spectrum consists of a singlet for the two equivalent selenium atoms at 148.6 ppm. Reactions with triphenylphosphine gold(I) chloride proceeded under similar conditions to yield $1,4-[(Ph_3P)AuSeC_6H_4SeAu(PPh_3)]$ 5a. Small, single crystals of 5a were obtained by diffusing npentane onto CH₂Cl₂ solutions, isolated as the CH₂Cl₂ solvate. The structural parameters are summarized in Table 2, and the crystallographic details are provided in the Experimental section (Table 3). The structure of 5a (Fig. 1) confirms the expected, near liner coordination about the Au(I) centres $(P-Au-Se = 178.95(8)^{\circ} \text{ for Au1 and } 175.26(9)^{\circ} \text{ for Au2}).$ The two Ph_3PAuSe units are nearly parallel (deviation = 1.1°), with each rotated out of the plane defined by the C_6 phenylene spacer by 99°.

Schmidbaur and co-workers (18) reported recently that treatment of phenylene-1,4-diol with $[{(p-CH_3C_6H_4)_3PAu}_3O][BF_4]$ in a 1:1 ratio leads to the formation of the tetragold dica-

Table 2. A summary of the bond lengths and angles.



Compounds	3b	5a	7b
Bond lengths (Å)			
a	1.88(1)	1.93(1)	1.94(1)
a'	1.88(1)	1.90(1)	1.91(1)
b	2.409(1)	2.408(1)	2.407(1)
b'	2.409(1)	2.401(2)	2.407(2)
с	2.271(2)	2.264(3)	2.274(4)
c′	2.271(2)	2.263(4)	2.265(4)
Bond angles (°)			
α	105.5(3)	103.2(4)	102.1(4)
α'	105.5(3)	103.5(4)	105.2(4)
β	173.47(7)	178.95(8)	179.6(1)
β′	173.47(7)	175.26(9)	178.4(1)

tionic complex 1,4-[{ $(p-CH_3C_6H_4)_3PAu$ }_2SC₆H₄S{Au(P-*p*-C₆H₄CH₃)₃}_2][BF₄]₂. This also leads to short intramolecular (3.16–3.21 Å) and intermolecular (2.97–3.16 Å) Au–Au interactions and an infinite chain-like arrangement of the 1,4-[(Au)_2SC₆H₄S(Au)_2]²⁺ repeat units (18). In **5a**, no significant Au···Au interactions are present, with distances (4.45 Å) significantly longer than the sum of the van der Waals radii (3.6 Å). A "head-to-tail" arrangement of adjacent Ph₃P-Au fragments leads to the crystallographic repeat observed in **5a**, with only weak interactions between adjacent 1,4-[(Ph₃P)AuSeC₆H₄SeAu(PPh₃)] (Au···Se = 3.37 and 3.54 Å) (Fig. 2).

The ¹H NMR spectra of biphenylene bridged 4,4'-[(EtPh₂P)AuSe(C₆H₄)₂SeAu(PPh₂Et)] **3b** and 4,4'-[(Ph₃P)AuSe(C₆H₄)₂SeAu(PPh₃)] **5b** display two doublets at 7.68 and 7.24 ppm, and 7.73 and 7.24 ppm, respectively, for the equivalent protons of the biphenylene rings. Consistent with the proposed structures, the ³¹P{¹H} NMR spectrum displays one signal for the equivalent phosphorus atoms (41.4 ppm for **3b** and 39.6 for **5b**), and the ⁷⁷Se{¹H} NMR spectrum shows the expected equivalence of the AuSe(C₆H₄)₂SeAu groups with one signal for each complex

	3b	5a	7b
Empirical formula	$C_{40}H_{38}Au_2P_2Se_2$	$C_{43}H_{36}Au_2Cl_2P_2Se_2$	$C_{30}H_{50}Au_2P_2Se_2$
Wavelength		0.710 73	
Temp (K)	295	150	150
Radiation type		Μο Κα	
Space group	P2(1)/n	P2(1)/c	<i>P</i> -1
a (Å)	13.214(1)	19.045(2)	8.4172(3)
<i>b</i> (Å)	9.9501(9)	15.0517(6)	12.6614(5)
c (Å)	14.366(1)	15.583(1)	17.4832(8)
α (°)			110.580(2)
β (°)	95.403(3)	113.930(1)	99.271(3)
γ (°)			95.174(3)
$\mu (mm^{-1})$	9.840	9.200	10.875
Diffractometer	Bruker APEX	Nonius Kappa CCD	Nonius Kappa CCD
<i>F</i> (000)	1068	2336	972
θ range (°)	2.00-26.37	2.34-27.55	2.48-27.70
Index ranges	$-13 \le h \le 16$	$-24 \le h \le 24$	$-10 \le h \le 10$
	$-12 \le h \le 11$	$-12 \le k \le 19$	$-16 \le k \le 16$
	$-17 \le k \le 16$	$-20 \le l \le 20$	$-22 \le l \le 22$
No. of reflns collected	8661	14974	14635
No. of ind. reflns	3843	9362	7776
<i>R</i> indices $[(I) > 2\sigma(I)]$	$R_1 = 0.0481$	$R_1 = 0.0657$	$R_1 = 0.0883$
	$wR_2 = 0.0591$	$wR_2 = 0.1521$	$wR_2 = 0.2332$
R indices (all data)	$R_1 = 0.0954$	$R_1 = 0.1612$	$R_1 = 0.1055$
	$wR_2 = 0.0654$	$wR_2 = 0.1976$	$wR_2 = 0.2485$
Refinement method	Full-matrix least-squares on F^2		
Refinement software	SHELXTL		

Table 3. Crystallographic data summary for complexes 3b, 5a, and 7b.

Fig. 1. A perspective view of the molecular structure of 1,4- $[(Ph_3P)AuSeC_6H_4SeAu(PPh_3)]$ **5a**. Thermal ellipsoids are drawn at the 40% probability level.



(**3b**: 157.0; **5b**: 156.6 ppm). The ${}^{31}P{}^{1}H{}$ NMR data are similar to those reported for related (triphenylphosphine)gold(I) thiolate and selenolate complexes (12, 19, 20, 21). The ${}^{77}Se$ NMR shifts of the biphenylene linked **3b** and **5b** resonate at higher field than their 1,4-phenylene linked counterparts **3a** and **5a**.

Crystals of 4,4'-[(EtPh₂P)AuSe(C₆H₄)₂SeAu(PPh₂Et)] **3b** were obtained from layering CH₂Cl₂ solutions with pentane. A summary of bond lengths and angles is provided in Table 2. Molecular **3b** resides about a crystallographic inversion centre (monoclinic space group $P2_1/n$), which bisects the atoms labelled C4-C4A (Fig. 3). The two C₆ rings are thus crystallographically co-planar and thus similar to the reported 4,4'-[Cl(Bu₃P)₂PdSe(C₆H₄)₂SePd(PBu₃)₂Cl] (17) and

Fig. 2. The packing of $1,4-[(Ph_3P)AuSeC_6H_4SeAu(PPh_3)]$ 5a in the crystal (hydrogen atoms omitted).



4,4'-[$(Cy_3P)AuS(C_6H_4)_2SAu(PCy_3)$] (18). The Au centres in **3b** deviate from linearity (173.47(7)) sightly more than was observed in **5a**. There are no significant intermolecular interactions.

Treatment of $(Me_2S)AuCl$ in THF solution with $Me_3SiSe(C_6H_4)_2SeSiMe_3$ (**2b**) at -78 °C produced an insoluble material (" $(Me_2S)AuSe(C_6H_4)_2SeAu(SMe_2)$ ") which can be used without isolation for the preparation of trialkylphosphine stabilized (R_3P)AuSe(C_6H_4)_2SeAu(PR_3). The addition of two equivalents of PPr₃ to a suspension of $(Me_2S)AuSe(C_6H_4)_2SeAu(SMe_2)$ (at -78 °C) resulted in a clear solution from which weakly diffracting single crystals

Fig. 3. A perspective view of the molecular structure of 4,4'-[(EtPh₂P)AuSe(C₆H₄)₂SeAu(PPh₂Et)] **3b**. Thermal ellipsoids are drawn at the 40% probability level.



Fig. 4. The molecular structure of 4,4'-[(Pr₃P)AuSe(C₆H₄)₂SeAu(PPr₃)] **7b**. Thermal ellipsoids are drawn at the 40% probability level.



of $4,4'-[(Pr_3P)AuSe(C_6H_4)_2SeAu(PPr_3)]$ 7b could be isolated. ¹H NMR spectra for **7b** display the expected signals for the equivalent propyl groups at 1.80, 1.58, 1.02 ppm with the aromatic resonances at 7.65 and 7.28 ppm, and in the ³¹P{¹H} NMR spectrum the equivalent phosphorus units gives rise to single signal at 32.5 ppm. The 77 Se{¹H} shows a singlet at 143.7 ppm. Attempts to prepare 4,4'-4.4'- $[(EtPh_2PAuSe(C_6H_4)_2SeAu(PPh_2Et)]]$ **3**b and $[(Ph_3PAuSe(C_6H_4)_2SeAu(PPh_3)]$ **5b** from ("(Me_2S)AuSe-(C₆H₄)₂SeAu(SMe₂)") via the addition of PPh₂Et were unsuccessful, as the suspended precipitate did not dissolve with the addition of the larger, less basic phosphine ligand in a variety of common organic solvents. Similarly, attempts to prepare 4,4'-[$(Pr_3P)AuSe(C_6H_4)_2SeAu(PPr_3)$] 7b from 4,4'-Me₃SiSe(C₆H₄)₂SeSiMe₃ 2b Pr₃PAu-Cl led to only poor yields of 7b.

X-ray diffraction analysis of single crystals of **7b** illustrate that the molecular geometry in the solid state is markedly different than that oberved for **3b** (Fig. 4). Unlike the planar C_6-C_6 structure observed in **3b**, the two phenylene rings in **7b** are rotated such that there is a 35.9° angle between them, similar to what was reported in 4,4'-[{(*p*-CH₃C₆H₄)₃PAuS-(C₆H₄)₂S{Au(P-*p*-C₆H₄CH₃)₃}₂]⁺ (40.3°). Unlike in **3b**, the P-Au-Se moieties asymmetrically lie on the same side of the biphenylene spacer, with a 42.4° angle between the two Se-Au-P vectors (Fig. 5). The Au-Se and Au-P distances are, however, similar to those oberved in **3b** and **5a** (Table 2).

In summary, the facile preparation of **3**, **5**, and **7b** from ligated Au-Cl and silylated selenium reagents has led to the first examples of dinuclear AuSe-spacer-SeAu. The strategies employed herein lend themselves to facile adaptation using didentate ligands (e.g., [ClAuPPh₂(CH₂)_xPh₂PAuCl]),

Fig. 5. A projection along the inter-ring C–C bond in 4,4'-[(Pr_3P)AuSe(C_6H_4)₂SeAu(PPr_3)] **7b** illustrating the orientation of the phenylene rings and the Au-Se-P moeities (propyl chains omitted).



which would allow for the preparation of coordination polymers (23) of the type $[AuPPh_2(CH_2)_xPh_2PAuSe(C_6H_4)_2Se]_n$. We are currently developing these avenues of research.

Experimental section

All syntheses were carried out under an atmosphere of high-purity dried nitrogen using standard double-manifold Schlenk line techniques and nitrogen-filled gloveboxes. Solvents were dried and collected using an MBraun MB-SP Series solvent purification system. Chloroform-d was dried and distilled over P₂O₅. NMR spectra [¹H (399.763 MHz), $^{13}C{^{1}H}$ (100.522 MHz), $^{77}Se{^{1}H}$ (76.217 MHz)] were recorded on a Varian Inova 400 NMR spectrometer. ¹H and ¹³C NMR chemical shifts were referenced internally to SiMe₄ using the residual proton and carbon signal of the deuterated solvent, respectively. ⁷⁷Se {¹H} spectra were referenced to external standards C₆H₅SeSiMe₃ at +85.6 ppm, relative to Me₂Se at 0 ppm. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, Canada). Crystals of 3b and 7b were mounted immersed in cooled mineral oil and placed in a cold stream of N2 during data collection. X-ray structural analyses were carried out on Bruker AXS (3b) and Enraf-Nonius Kappa CCD (5a and 7b) single-crystal X-ray diffractometers. Data were corrected for Lorentz and polarization effects. The SHELXTL (G.M. Sheldrick, Madison, Wisconsin, USA) program package was used to solve (direct methods, Au, Se, and P) and refine the structures. The weighting scheme employed was of the form $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ (a, b = refined variables, $P = 1/3 \max(F_0^2, 0) + 2/3 F_c^2$). All non-hydrogen atoms, with the exception of disordered carbon centers, were refined with anisotropic thermal parameters. Hydrogen atoms were included as riding on their respective carbon atoms. The structures solved and refined without complications, with the following exceptions: In 3b, a solvent moleceule of crystallization (CH₂Cl₂) was refined as disordered over two sites with restrained geometries; in 7b, many of the carbon atoms of the propyl chains were disordered over two sites. A satisfactory model with 50:50 occupancy was refined using mild restraints (SADI command). All nonhydrogen atoms, with the exception of disordered carbon centres, were refined with anisotropic thermal parameters.

Hydrogen atoms were included as riding on their respective carbon atoms.⁴

Materials

Phenylene-1,4-bis(trimethylsilylselenium) and biphenylene-4,4'-bis(trimethylsilylselenium) (17), [AuCl(SMe₂)] (22), and R₃PAuCl (23) were synthesized according to literature procedures.

Synthesis of EtPh₂PAuSeC₆H₄SeAuPPh₂Et (3a)

EtPh₂PAuCl (220.7 mg, 0.494 mmol) was added in one portion to 1,4-C₆H₄(SeSiMe₃)₂ (94.0 mg, 0.247 mmol) in tetrahydrofuran (30 mL) at -78 °C and warmed to room temperature (RT) after 15 min. After 2 h of stirring at RT, all volatiles were removed in vacuo, and the residue obtained was washed with *n*-pentane. Crystallization from *n*pentane/dichloromethane (8:1) gave yellow crystals of **3a** in 72% yield (188 mg, 0.178 mmol). ¹H NMR (CDCl₃) δ : 7.65 (m, 12 H, C₅H₄), 7.46 (m, 8 H, C₅H₄), 7.41 (s, 4 H, C₆H₄), 2.44 (dq, 4 H, J_{HH} = 8 Hz, J_{HP} = 16 Hz, CH₂), 1.23 (dt, 6 H, J_{HH} = 8 Hz, J_{HP} = 20 Hz, CH₂). ¹³¹P{¹H} δ : 38.9. ⁷⁷Se{¹H} δ : 148.6. Anal. for C₃₄H₃₄Au₂P₂Se₂ (1056.43): found: C 37.75, H 3.43; calcd.: C 38.65, H 3.24.

Synthesis of EtPh₂PAuSe(C₆H₄)₂SeAuPPh₂Et (3b)

One hundred mg of 4,4'-(C_6H_4 SeSiMe₃)₂ (0.219 mmol) was reacted with 196 mg (0.438 mmol) of EtPh₂PAuCl as described for the preparation of **3a** (above). After appropriate work-up, **3b** was isolated as yellow crystals in 75% yield (186 mg, 0.164 mmol). ¹H NMR (CDCl₃) δ : 7.68 (d, 4 H, $J_{\rm HH} = 8$ Hz, C_6H_4), 7.65 (m, 12 H, C_5H_4), 7.45 (m, 8 H, C_5H_4), 7.24 (d, 4 H, $J_{\rm HH} = 8$ Hz, C_6H_4), 2.45 (dq, 4 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.23 (dt, 6 H, $J_{\rm HH} = 8$ Hz, $J_{\rm HP} = 20$ Hz, CH_2), 1.31P{¹H} δ : 41.4. ⁷⁷Se{¹H} δ : 157.0. Anal. for C₄₀H₃₈Au₂P₂Se₂ (1132.52): found: C 42.18, H 3.36; calcd.: C 42.42, H 3.38.

Synthesis of Ph₃PAuSeC₆H₄SeAuPPh₃ (5a)

One hundred mg of $1,4-C_6H_4(\text{SeSiMe}_3)_2$ (0.263 mmol) was reacted with 260 mg (0.526 mmol) of Ph₃PAuCl as described for the preparation of **3a** (above). After appropriate work-up, **3b** was isolated as a yellow solid in 71% yield (216 mg, 0.187 mmol). ¹H NMR (CDCl₃) δ : 7.47 (m, 30 H, C_6H_5), 7.42 (s, 4 H, C_6H_4). ¹³¹P{¹H} δ : 39.9. ⁷⁷Se{¹H} δ : 148.2. Anal. for $C_{42}H_{34}Au_2P_2Se_2$ (1152.52): found: C 43.49, H 2.93; calcd.: C 43.77, H 2.97.

Synthesis of $Ph_3PAuSe(C_6H_4)_2SeAuPPh_3$ (5b)

One hundred mg of 4,4'-(C_6H_4 SeSiMe₃)₂ (0.219 mmol) was reacted with 217 mg (0.438 mmol) of Ph₃PAuCl as described for the preparation of **3a** (above). After appropriate work-up, **3b** was isolated as yellow solid in 73% yield (196 mg, 0.160 mmol). ¹H NMR (CDCl₃) δ : 7.73 (d, 4 H, $J_{\rm HH} = 8$ Hz, C_6H_4), 7.53 (m, 18 H, C_6H_5), 7.43 (m, 12 H, C_6H_5), 7.24 (d, 4 H, $J_{\rm HH} = 8$ Hz, C_6H_4). ¹³¹P{¹H} δ : 39.6.

⁷⁷Se{¹H} δ: 156.6. Anal. for $C_{48}H_{38}Au_2P_2Se_2$ (1228.62): found: C 46.54, H 2.99; calcd.: C 46.92, H 3.12.

Synthesis of $Pr_3PAuSe(C_6H_4)_2SeAuPPr_3$ (7b)

[AuCl(SMe₂)] (65 mg, 0.221 mmol) was added in one portion to 4,4'-(C₆H₄SeSiMe₃)₂ (51 mg, 0.111 mmol) in tetrahydrofuran (30 mL) at -78 °C and warmed to RT after 15 min. After 2 h of stirring at RT, a yellow suspension formed. The reaction mixture was again cooled to -78 °C, and 0.43 mL of PPr₃ (35.4 mg, 0.221 mol) was added in one portion to the reaction mixture. After 2 h of stirring at RT, all volatiles were removed in vacuo from the clear yellow solution, and the residue obtained was washed with *n*pentane. Crystallization from *n*-pentane/dichloromethane (8:1) gave colorless crystals of **7b** in 75% yield (79 mg, 0.083 mmol). ¹H NMR (CDCl₃) δ : 7.65 (d, 4 H, J_{HH} = 8 Hz, C₆H₄), 7.23 (d, 4 H, J_{HH} = 8 Hz, C₆H₄), 1.80 (m, 12 H, CH₂CH₂CH₃), 1.58 (m, 12 H, CH₂CH₂CH₃), 1.02 (m, 18H, CH₂CH₂CH₃). ¹³¹P{¹H} δ : 32.5. ⁷⁷Se{¹H} δ : 143.7.

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References

- H.G. Raubenheimer and S. Cronje. *In* Gold, progress in chemistry, biochemistry and technology. *Edited by* H. Schmidbaur. Wiley, Chichester, NY, USA. 1999. p. 557.
- 2. C.F. Shaw III. Chem. Rev. 99, 2589 (1999).
- 3. S.L. Best and P.J. Sadler. Gold Bull. 29, 2987 (1996).
- 4. M.J. McKeage, L. Maharaj, and S.J. Berners-Price. Coord. Chem. Rev. 232, 127 (2002).
- 5. E.R.T. Tiekink. Crit. Rev. Oncol/Hematol. 42, 225 (2002).
- S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, and A. Laguna, Inorg. Chem. 43, 7234 (2004).
- 7. P.G. Jones and C. Thöne. Chem. Ber. 123, 1975 (1990).
- W. Eikens, C. Kienitz, P.G. Jones, and C. Thöne. J. Chem. Soc. Dalton Trans. 83 (1994).
- (a) R.J. Puddephatt and P.J. Thompson. J. Organomet. Chem. 117, 396 (1976); (b) S. Canales, O. Crespo, M.-C.Gimeno, P.G. Jones, A. Laguna, and P. Romero. J. Chem. Dalton Trans. 4525 (2003).
- A. Laromaine, F. Teixidor, R. Kivekäs, R. Sillanpää, M. Arca, V. Lippolis, E. Crespo, and C. Viñas. J. Chem. Soc. Dalton Trans. 5240 (2006).
- P.J. Bonasia, D.E. Cindelberger, and J. Amold. Inorg. Chem. 32, 5126 (1993).
- 12. I. Wagner and W.-W. du Mont, J. Organomet. Chem. **395**, C23 (1990).
- E. Cerrada, S. Elipe, M. Laguna, F. Lahoz, and A. Moreno. Synth. Met. **102**, 1759 (1999).

⁴ Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3861. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 696168–696170 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

- 14. S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, and A. Laguna. Inorg. Chem. 43, 7234 (2004).
- 15. W. Eikens, C. Kienitz, P.G. Jones, and C. Thöne. J. Chem. Soc. Dalton Trans. 83 (2004).
- P.J. Bonasia, D.E. Cindelberger, and J. Arnold. Inorg. Chem. 32, 5126 (1993).
- 17. A.I. Wallbank, M.J. Brown, C. Nitschke, and J.F. Corrigan. Organometallics, 23, 5648 (2004).
- H. Ehlich, A. Schier, and H. Schmidbaur. Inorg. Chem. 41, 3721 (2002).
- 19. P.G. Jones and C. Thöne. Chem. Ber. 123, 1975 (1990).
- 20. P.G. Jones and C. Thöne. Chem. Ber. 124, 2725 (1991).
- 21. P.G. Jones and C. Thöne. Inorg. Chim. Acru, 181, 291 (1991).
- 22. M.-C. Brandys, M.C. Jennings, and R.J. Puddephatt. J. Chem. Soc. Dalton Trans. 4601 (2000).
- 23. A.A. Isab, M.B. Fettouhi, S. Ahmad, and L. Ouahab. Polyhedron, 22, 1349 (2003).