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# Synthesis, X-ray molecular structure analysis, and study on ligand scrambling reactions of new thiolatogold(I) complexes with various phosphines

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### Abstract

Treatment of Au(PPh<sub>3</sub>)Cl, (AuCl)<sub>2</sub>(*trans*-dpen) and (AuCl)<sub>2</sub>(dppfe) with Sn(SPh)(*n*-Bu)<sub>3</sub> and/or PhSH/KOH affords Au(PPh<sub>3</sub>)(SPh) (1), (AuSPh)<sub>2</sub>( $\mu$ -*trans*-dpen) (2), (AuSPh)2( $\mu$ -dppfe) (3), (AuSPh)( $\mu$ -*trans*-dpen)(AuCl) (4), and (AuSPh)-( $\mu$ -dppfe)(AuCl) (5) in good yields. All these thiophenolates are characterized by single crystal X-ray analysis, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. 1 forms tetramer through Au···Au interaction and  $\pi$ - $\pi$  interaction between the phenyl group in SPh and one of the phenyl groups in PPh<sub>3</sub> in the solid state. An infinite chain structure is formed for 2 through intermolecular aurophilicity and these chains are connected by partial overlap ( $\pi$ - $\pi$  interaction) of neighboring phenyl groups in SPh to give two-dimensional networks in the solid state. Similar infinite chains are formed through aurophilicity, but two-dimensional networks are not formed for 4 in the solid state. No multidimensional structure is formed for 3 and 5 in the solid state. <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy of CDCl<sub>3</sub> solutions of 2, 3, 4, and 5 has revealed that rapid ligand scrambling takes place for 4 and 5. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiolatogold(I) complexes; Au-Au interaction; Infinite chain structures; Ligand scrambling

### 1. Introduction

There is a continuing interest in the coordination chemistry of thiolatogold(I) complexes for several reasons. Among these are the relevance to biological systems especially to drugs [1-7], the usage of the gold complexes as lubrication additives [8,9], and the application to supramolecular chemistry [10,11]. Applications for thiolatogold complexes have surged in the fields of nanoparticles, nanostructured films, modem electronics, and opto-electonics [12–17]. For the satis-

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factory understanding of the structures and bonding of these thiolatogold nanoparticles, nano-clusters and surface chemistry, it appears that the systematic study of the chemistry of simple thiolatogold(I) complexes is inevitable. However, to our surprise, there has not been enough exploration for targeting this field of chemistry [18,19]. Another interesting feature of the thiolatogold(I) complexes is that they will provide an excellent opportunity for inducing the Au-Au interaction (aurophilicity) in the solid [20], because recent theoretical studies by Pyykkö et al. have suggested that the aurophilic interaction is augmented by introducing a SR (thiolate) group to a gold(I) complex [21]. Thus supramolecular chemistry and/or the design of extended solid state structural chemistry have been burgeoning for the past decade with the aid of the aurophilic

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interaction [21-28]. In most of these studies, only the force of the aurophilic interaction has been used to construct multidimensional arrays in solid states. However, Schmidbaur et al. has recently successfully assembled the L-Au-X units into supramolecular arrays in the solid-state by collaborating two weak interactions, that is, aurophilic interaction and hydrogen bonding [23]. We have imagined that the collaboration of similar weak interactions such as  $\pi - \pi$  interaction with aurophilic interaction may also bring an extended solidstate structure. We are now able to present four examples of the type  $(Au-L)(\mu-diphos)(Au-X)$  where L represents thiophenol and X thiophenol and/or chloride [29]. The present paper reports on the synthesis, X-ray molecular structure analysis, and the ligand scrambling reactions in solutions of thiolatogold(I) complexes together with X-ray structure analysis on the molecular structure and the crystal packing of Au(SPh)PPh<sub>3</sub>, the crystal structure of which was reported in 1993 by Schmidbaur et al. and in 1994 by Fackler et al. without information on crystal packing [30].

### 2. Experimental

### 2.1. General procedure

All reactions were carried out under a purified nitrogen atmosphere using Schlenk and vacuum line techniques. Solvents were dried by standard methods and distilled under nitrogen. Dppfe (dppfe = 1, 1'-bis(diphenylphosphino)ferrocene) and cis-dpen (dpen = 1,2-bis(diphenylphosphino)ethylene) were purchased from Strem Chemicals and trans-dpen was purchased from Aldrich. HAuCl<sub>4</sub> was purchased from Tanaka Precious Metals Co. PhSH and PPh3 were obtained  $(AuCl)_2(\mu$ -cis-dpen), from Wako Chemicals.  $(AuCl)_2(\mu$ -trans-dpen),  $(AuCl)_2(\mu$ -dppfe) and Au(PPh<sub>3</sub>)Cl were prepared by literature methods [31-34]. (n-Bu)<sub>3</sub>SnSPh was prepared as previously reported [35].

# 2.2. Synthesis of Au(SPh)PPh<sub>3</sub> (1)

A 445 mg sample (0.90 mmol) of AuCl(PPh<sub>3</sub>) was suspended in THF (60 ml) and to this was added a slight excess of  $(n-Bu)_3$ SnSPh (425 mg, 1.07 mmol). The mixture was refluxed for 20 h. Then the solvent was distilled off at reduced pressure to leave a pale yellow oil. The oil was treated with a small amount of hexane to remove some soluble components and the residue was extracted with benzene. A white solid was left upon distillation of the benzene and this was recrystallized from benzene–hexane (1:1) to afford single crystals of Au(SPh)PPh<sub>3</sub> (1) (yield 475 mg, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.43–7.63 (m, 17H, PPh, m-SPh), 6.99 (t, 2H, *o*-SPh), 7.11 (t, 1H, *p*-SPh).  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$  39.2 (s). These NMR data are close to those reported by Schmidbaur et al [30]. *Anal.* Calc. for C<sub>24</sub>H<sub>20</sub>AuPS: C, 50.71; H, 3.55. Found: C, 50.47; H, 3.48%.

# 2.3. Synthesis of (AuSPh)<sub>2</sub>{trans-1,2-bis(diphenylphosphino)ethylene} (2)

A similar procedure to that of 1 was employed. To a THF suspension (20 ml) of  $(AuCl)_2(\mu$ -trans-dpen) (215 mg, 0.25 mmol) was added (n-Bu)<sub>3</sub>SnSPh (196 mg, 0.49 mmol) and the mixture was refluxed for 2.5 h. After being cooled to room temperature (r.t.), the solvent was distilled at reduced pressure to leave a pale yellow solid. This solid was washed with hexane (25 ml) and then with benzene (70 ml) and the pale yellow residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 ml). The solvent was vacuum-stripped from the extract to leave pale-yellow solid of 2 (yield 194 mg, 79%). Single crystals for X-ray analysis were grown from CH<sub>2</sub>Cl<sub>2</sub>-hexane. 2 was also obtained from the reaction of  $(AuCl)_2(\mu$ -cis-dpen) with PhSH and KOH in CH<sub>2</sub>Cl<sub>2</sub>-acetone in similar yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270MHz): δ 7.46–7.65 (m, 24H, PPh, m-SPh), 6.94-7.08 (m, 6H, o-SPh, p-SPh), 7.29 (t, 2H,  $J_{P-H} = 18.8$  Hz, HC=). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ 35.87 (s). Anal. Calc. for C<sub>38</sub>H<sub>32</sub>Au<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 45.25; H, 3.20. Found: C, 44.73; H, 3.14%.

# 2.4. Synthesis of (AuSPh)<sub>2</sub>{μ-1,1'-bis(diphenylphosphino)ferrocene} (3)

A similar procedure to that of 1 was employed. A 611 mg (0.6 mmol) sample of  $(AuCl)_2(\mu$ -dppfe) was dissolved in THF (25 ml) and to this was added 499 mg (1.25 mmol) of (n-Bu)\_3Sn(SPh). The yellow solution was refluxed for 2.5 h. After being cooled to r.t., the resulting yellow precipitates were collected on a frit and washed with THF (20 ml) and then with petroleumether (20 ml) to leave 587 mg, (84%) of **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.38–7.54 (m, 20H, PPh), 7.09–7.14 (m, 4H, *o*-SPh), 7.60–7.65 (m, 4H, *m*-SPh), 6.99 (t, 2H, *p*-SPh), 4.18–4.20 (m, 4H, C<sub>2</sub>-*H* in Cp), 4.64–4.65 (m, 4H, C<sub>3</sub>-*H* in Cp). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  32.80 (s). *Anal.* Calc. for C<sub>46</sub>H<sub>38</sub>Au<sub>2</sub>FeP<sub>2</sub>S<sub>2</sub>: C, 47.36; H, 3.28%. Found: C, 46.77; H, 3.31%.

# 2.5. Synthesis of (AuSPh)(μ-trans-1,2bis(diphenylphosphino)ethylene}(AuCl) (4)

An 861 mg (1.0 mmol) sample of  $(AuCl)_2(\mu$ -transdpen) was dissolved in a mixed solvent of  $CH_2Cl_2$  (60 ml) and acetone (50 ml). To this was added a MeOH solution (30 ml) of PhSH (110 mg, 1.0 mmol) and KOH (28 mg, 0.53 mmol) and the mixture was stirred at r.t. for several hours. The solvent was distilled off at reduced pressure to leave pale yellow solid. This solid was recrystallized from benzene to afford pale yellow crystals of **4**. Yield 360 mg (41%). **4** was also obtained from the reaction of  $(AuCl)_2(\mu$ -cis-dpen) with PhSH and KOH in CH<sub>2</sub>Cl<sub>2</sub>-acetone in a similar yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.48–7.63 (m, 22H, PPh, *m*-SPh), 6.95–7.08 (m, 3H, *o*-SPh, *p*-SPh), 7.22 (t, 2H, *J*<sub>P</sub>-H=19.3 Hz, *H*C=). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  32.64 (s). *Anal.* Calc. for C<sub>32</sub>H<sub>27</sub>Au<sub>2</sub>ClP<sub>2</sub>S: C, 41.11; H, 2.91. Found: C, 40.04; H, 2.97%.

### 2.6. Synthesis of

### (*AuSPh*){[ $\mu$ -1,1'-bis(diphenylphosphino)ferrocene} (*AuCl*) (**5**)

To a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub> (30 ml) and acetone (25 ml),  $(AuCl)_2(\mu$ -dppfe) (510 mg, 0.5 mmol) was dissolved. A methanol solution of PhSH (55 mg, 0.5 mmol) and KOH (30 mg, 0.5 mmol) was added to this solution and the mixture was stirred for several hours. The solvents were vacuum-stripped to leave an orange product. The product was washed with 20 ml of hexane and extracted with benzene (50 ml). The distillation of benzene from the extract afforded the orange product **5**. Yield 470 mg, 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.41–7.54 (m, 20H, PPh), 7.12 (t, 2H, *o*-SPh), 7.62–7.65 (m, 2H, *m*-SPh), 6.99 (t, 1H, *p*-SPh), 4.22–4.25 (m, 4H, C<sub>2</sub>-*H* in Cp), 4.68 (s, 4H, C<sub>3</sub>-*H* in Cp). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  30.43 (s).

## 2.7. X-ray crystallography on 1, 2, 3, 4, and 5

Suitable crystals of these five compounds were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane. The selected crystals were glued to the top of a fine glass rod. Accurate cell dimensions were obtained by leastsquare refinements of 22-25 reflections on a MAC MXC3 diffractometer equipped with graphitemonochromated Mo Ka radiation. The reflection data were collected at r.t. for 1, 2, and 3 and at  $-100^{\circ}$ C for 4 and 5 by use of an Oxford cryostream cooler. Complete crystal data are given in Table 1. The structures of 1 and 2 were solved by the direct method, Dirdif, and that of 3 by SIR92 in a Crystan-GM program package and those of 4 and 5 by SHELXS86 in a Crystan program package; these program packages were provided by MAC Science. An analytical absorption correction was applied for 4 and 5 [36]. The structures were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms except 2, 4, and 5 by an aforementioned Crystan-GM and a Crystan program package. Refinements were made anisotropically for heavy atoms and isotropically for carbon atoms in 2, 4, and 5, because anisotropic refinements for carbon atoms made the thermal parameters negative for more than ten carbon atoms for these compounds; carbon atoms in all the phenyl rings of 2 were refined as rigid ring atoms. We repeated the processes and methods for recrystallization many times to obtain good quality crystals. The crystals used for measurements were the best ones so far. The final Rand  $R_w$  values are also listed in Table 1. At first we suspected that a small amount of impurities contained in the crystals as a result of co-crystallization rather than imperfection of the crystals should be responsible for high values of R for 2, 3, and 5 as was suggested previously by Parkin and Rheingold [37]. As was described in the Section 2, elemental analysis on 4 has given less satisfactory results, but the R value is rather satisfactory. Instead, R values for 2 and 3 which show satisfactory elemental analyses are high. It is difficult at present for us to conclude which factor is responsible for high R values for these crystals. Tables for atomic coordinates, thermal parameters, and bond lengths and angles are available as supporting information. Selected bond-lengths and angles are shown in Tables 2-6.

# 2.8. NMR study on ligand-exchange reactions in a solution

Solutions of 3, 5 (5.0 and 20.0 mmol) and  $(AuCl)_2(\mu$ dppfe) (6) in  $CDCl_3$  were subjected to the measurement of <sup>31</sup>P{<sup>1</sup>H} NMR spectra and similarly prepared 1.0 and 10.0 mmol solutions of 3, 5 and 6 were employed for <sup>1</sup>H NMR spectral measurements to assay the concentration effect. For 2 and 4, 1.0, 5.0 and 20.0 mmol solutions in CDCl<sub>3</sub> were used for <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectral measurements, while only the 3.0 mmol solution of  $(AuCl)_2(\mu$ -trans-dpen) (7) was used because of low solubility in CDCl<sub>3</sub>. Deuterated THF was also used for NMR measurements of 2, 4, and 5 to explore the solvent effect on the ligand scrambling. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-2000 (300 MHz) and/or JEOL FT/EX-270 (270 MHz) spectrometer and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 80.984 MHz on a Varian XL-200 spectrometer equipped with a temperature controller. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>.

### 3. Results and discussion

### 3.1. Synthesis

Replacement of two Cl groups in  $(AuCl)_2(\mu$ -diphos) has been achieved by two methods, that is, the reaction with Sn(SPh)(*n*-Bu)<sub>3</sub> and the reaction with HSPh– KOH; the use of Sn(SPh)(*n*-Bu)<sub>3</sub> for replacement of the halogen by the SPh group has precedent in the synthesis of Mn<sub>4</sub>(SPh)<sub>4</sub>(CO)<sub>12</sub> from Mn<sub>2</sub>(CO)<sub>8</sub>Br<sub>2</sub> and Sn-

Table 1	
Crystal	data

Compound	AuSPh(PPh <sub>3</sub> ) (1)	$(AuSPh)_2$ ( $\mu$ -trans-dpen) (2)	(AuSPh) <sub>2</sub> ( <i>µ</i> -dppfe) ( <b>3</b> )	(AuSPh)(µ-trans-dpen) (AuCl) (4)	$(AuSPh)(\mu$ -dppfe)(AuCl)· CH <sub>2</sub> Cl <sub>2</sub> ( <b>5</b> )
Formula	C <sub>24</sub> H <sub>20</sub> AuPS	$C_{38}H_{32}Au_2P_2S_2$	$C_{46}H_{38}Au_2FeP_2S_2$	$C_{32}H_{27}Au_2ClP_2S$	C40H33AuClP2S
Formula weight	568.4	1008.6	1166.6	934.9	1177.8
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	Aa	<i>P</i> 1
$a(\mathbf{A})$	11.552(3)	12.527(3)	10.147(4)	15.520(4)	12.391(6)
$b(\mathbf{A})$	16.766(4)	15.383(2)	13.032(6)	19.010(5)	20.035(7)
c (Å)	11.030(2)	9.740(1))	8.652(3)	11.715(4)	8.479(3)
α (°)	93.51(2)	96.55(1)	106.32(4)		92.58(3)
β (°)	93.23(2)	91.95(2)	105.62(3)	108.73(2)	103.83(3)
γ (°)	97.00(2)	70.50(2)	101.80(4)		76.45(4)
$V(Å^3)$	2112.1(8)	1757.8(6)	1007.8(7)	3273(2)	1987(1)
Ζ	4	2	1	4	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.79	1.91	1.92	1.90	1.83
Crystal dimensions (mm <sup>3</sup> )	$0.45 \times 0.25 \times 0.20$	$0.25 \times 0.20 \times 0.20$	$0.45 \times 0.20 \times 0.05$	$0.40 \times 0.20 \times 0.20$	$0.55 \times 0.25 \times 0.15$
$\mu$ (Mo K $\alpha$ ) <sup>a</sup> (cm <sup>-1</sup> )	41.15	46.30	41.8	50.0	42.3
Scan type	$2\theta - \omega$	ω	$2\theta - \omega$	$2\theta - \omega$	ω
Scan range	$1.50 + 0.35 \tan \theta$	$1.55 + 0.35 \tan \theta$	$1.65 + 0.35 \tan \theta$	$1.70 + 0.35 \tan \theta$	$2.60 + 0.35 \tan \theta$
Scan speed (° $min^{-1}$ )	6.0	5.0	5.0	6.0	6.0
$2\theta_{\rm max}$ (°)	50.0	50.0	50.0	55.0	45.0
Temperature (K)	298	298	298	173.2	173.2
Unique reflections	5516	5519	3551	3758	5175
Reflections with $ F_{\alpha}  > n\sigma( F_{\alpha} )$	4541 ( <i>n</i> = 4)	3941 ( <i>n</i> = 3)	2981 ( <i>n</i> = 4)	2518 ( <i>n</i> = 3)	3044 ( <i>n</i> = 4)
No. of parameters refined	487	403	247	187	246
R <sup>b</sup>	0.075	0.091	0.126	0.067	0.114
$R_w^{c}$	0.113	0.137	0.154	0.10	0.141

<sup>a</sup> Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å).

<sup>b</sup>  $R = \Sigma ||F_{o}| - |F_{c}|| / |F_{o}|.$ 

 $^{c}R_{w} = [\Sigma(|F_{o}| - |F_{c}|)^{2}/\Sigma w(F_{o})^{2}]^{1/2}$  where  $w = 1/\sigma^{2}(F)$ .

 $(SPh)(n-Bu)_3$  [37,38]. The yields of the product by both methods are comparable and are relatively high. 1 was synthesized previously from the reaction of Ph<sub>3</sub>PAuCl with PhSH and Et<sub>3</sub>N by Shmidbaur et al., but the yield was less satisfactory compared with that of our methods [30]. Substitution of SPh for one Cl has been made by the latter method to obtain 4 and 5. This is the first report on the synthesis of  $(AuSR)(\mu$ -diphos)(AuCl) type mixed thiolatogold complexes to the best of our knowledge. However, the yield of mono-substituted 4 is less satisfactory. The reason has been lately clarified by NMR study on the facile ligand scrambling reaction of the monosubstituted product in solution. Results on elemental analyses for 1-3 are satisfactory, but the results on 4 are rather unsatisfactory; the finding suggests that small amounts of impurities should be contained in the crystals. Elemental analysis of 5 has not yet been made. Attempts to substitute SPh for Cl in  $(AuCl)_2(\mu$ -cis-dpen) with PhSH and/or Sn(SPh)(n-Bu)<sub>3</sub> have shown that the cis-backbone is isomerized to the

Table 2 Selected bond-lengths (Å) and angles (°) of 1

Au1–Au2	3.145(2)	Au1–S1	2.30(1)
Au2–P2	2.28(1)	S1-C1	1.77(4)
P1-C31	1.78(4)	P1-C41	1.81(3)
P2-C71	1.71(4)	Au1–P1	2.263(9)
Au2–S2	2.32(1)	P1-C21	1.82(3)
S2-C7	1.79(4)	P2-C61	1.81(5)
P2-C51	1.89(4)		
S1-Au1-P1	175.9(4)	S2–Au2–P2	179.3(4)
Au2-Au1-P1	103.5(3)	Au1-Au2-S2	77.8(3)
Au1-S1-C1	109(1)	Au2-S2-C7	107(1)
Au1-P1-C31	116(1)	Au1-P1-C41	111(1)
Au2-P2-C61	112(2)	Au2-P2-C71	115(1)
Au2-Au1-S1	75.9(3)	Au1-Au2-P2	102.7(3)
Au1-P1-C21	116(1)	Au2-P2-C51	110(3)
P1-Au1-Au2-P2	100.3(4)		
(torsional angle)			

Table 3							
Selected	bond-lengths	(Å)	and	angles	(°)	of	2

Au1–Au2	3.023(2)	Au1–S1	2.33(2)
Au2–P2	2.18(2)	C1–C	1.29(6)
S2-C31	1.67(1)	P1C1	1.83(5)
P1-C23	1.80(5)	P2-C2	1.89(7)
Au2–S2	2.24(3)	Au1–P1	2.27(1)
C2-C2′	1.32(9)	S1-C11	1.78(6)
P2-C2	1.89(7)	P1-C17	1.67(5)
P2-C37	1.7(1)	P2-C43	1.79(7)
S1-Au1-P1	173.4(6)	Au1-S1-C11	100(2)
Au2-S2-C31	112(6)	Au2-P2-C2	113(2)
C1-P1-C17	116(2)	C2-P2-C37	106(3)
C2-P2-C43	101(3)	P2-C2-C2'	120(5)
S2-Au2-P2	176.4(6)	C1-P1-C23	102(2)
Au1-P1-C1	111(2)	P1-C1-C1'	120(3)
S1-Au1-Au2-S2 (torsional angle)	106.2		

Table 4

Selected bond-lengths (Å) and angles (°) of  $\mathbf{3}$ 

Au1–S1	2.316(9)	Fe1–C1	2.01(3)
Fe1-C3	2.07(4)	Fe1-C5	2.04(4)
P1-C1	1.76(3)	P1-C18	1.87(3)
Au1–P1	2.274(8)	Fe1-C2	2.05(4)
Fe1-C4	2.05(4)	S1-C6	1.77(4)
P1-C12	1.82(3)		
S1-Au1-P1	170.7(3)	Au1-P1-C1	117(1)
Au1-P1-C12	106.8(9)	Au1-P1-C18	114(1)
Au1-S1-C6	102(2)		

Table 5

Selected bond-lengths (Å) and angles (°) of 4

Au1–Au2	3.093(2)	Au1–P1	2.27(1)
Au1–C11	2.32(2)	S1-C5	1.86(7)
P2-C2	1.93(4)	P1-C17	1.81(5)
P2-C29	1.86(3)	Au2–P2	2.21(1)
Au2–S1	2.23(1)	P1-C1	1.65(4)
C1-C2	1.38(6)	P2-C23	1.82(3)
P1-C11	1.84(5)		
Au1-Au2-S1	82.0(6)	Au2-Au1-P1	103.6(5)
Au2-Au1-C11	79.7(6)	Au1-P1-C1	118(1)
Au2-P2-C2	109(1)	Au2-S1-C5	97(2)
Au1-P1-C11	105(2)	Au2-P2-C23	122(1)
Au2-P2-C29	114(1)	P1-Au1-C11	174.3(7)
Au1-Au2-P2	102.0(4)	Au1-P1-C17	98(2)
S1-Au2-P2	175.2(7)		

*trans*-backbone and  $(Au-SPh)_2(\mu$ -*trans*-dpen) (2) is produced. Similar attempts to synthesize  $(AuSPh)(\mu$ -*cis*-dpen)(AuCl) have yielded the *trans* isomer 4. Reactions have been carried out with a simple method of shielding from light. Rigorous shielding from light seems necessary to yield *cis*-isomers as was demonstrated by Bruce et al. for photo-isomerization of  $(AuX)_2(\mu$ -*cis*-dpen) to  $(AuX)_2(\mu$ -*trans*-dpen) [39].

### 3.2. Molecular structure

The final *R* factors for 2, 3, and 5 are relatively high because of the poor quality of the crystals used for measurements. The results, however, are satisfactory for our purposes to ascertain the existence of aurophilicity and to explore supra-structures in solid states. The reason why it is difficult to obtain good quality crystals will be discussed later. The molecular structures presented by ORTEP drawings are shown in Figs. 1-5. The structure of 1 (Fig. 1) was solved as a dimer; the Au…Au distance is 3.145(2) Å, which indicates an aurophilic interaction [20-28]; the geometry of 1 is essentially identical to that reported by Shmidbaur et al. and Fackler et al. (r(Au-Au) = 3.1355(3)) and 3.154(2) Å) [30]. The structure of 2 was also solved and refined as a dimer (Fig. 2); the Au. Au distance is 3.023(2) A. This distance also indicates an aurophilic interaction [20-28]. The structure of 3 was solved and

Selected	bond-lengths	(Å) and	angles (°) of 5	
		( )		

Au1–P1	2.25(1)	Au2–P2	2.26(1)
Fe1-C1	2.06(5)	Fe1-C3	1.95(5)
Fe1–C5	2.03(4)	Fe1-C7	2.02(5)
Fe1–C9	2.05(6)	S1-C11	1.59(9)
P1-C17	1.82(4)	P2-C6	1.78(5)
P2-C37	1.84(4)	Au2–S1	2.28(2)
Au1–C11	2.29(2)	Fe1–C4	2.01(5)
Fe1–C2	2.09(5)	Fe1–C8	2.07(5)
Fe1–C6	2.02(5)	P1-C1	1.78(5)
Fe1-C10	2.11(5)	P2-C31	1.84(5)
P1-C23	1.82(5)		
P1-Au1-C11	177.0(5)	Au1–P1–C1	111(2)
P2-Au2-S1	176.4(5)	Au1–P1–C17	117(2)
Au2-P2-C6	115(2)	Au2-P2-C37	112(2)
Au1-P1-C23	106(2)	Au2-P2-C31	112(2)
Au2-S2-C11	114(2)		



Fig. 1. The ORTEP drawing of  $Au(PPh_3)(SPh)$  (1) which shows the dimer structure.



Fig. 2. The ortep drawing of  $(AuSPh)_2(\mu$ -trans-dpen) (2) which shows the dimer structure.



Fig. 3. The ORTEP drawing of (AuSPh)<sub>2</sub>(µ-dppfe) (3).



Fig. 4. The ORTEP drawing of (AuSPh)(µ-trans-dpen)(AuCl) (4).

refined for a single molecule (Fig. 3). Two Au-SPh groups are in a staggered conformation  $(180^\circ)$  and thus an intramolecular aurophilic interaction is impossible. The molecular structure of **4** was solved and refined for a single molecule (Fig. 4). The Au-SPh group and the

Au-Cl group are in a trans position. Therefore, intramolecular aurophilic interaction is impossible. The molecular structure of 5 was also solved and refined for a single molecule. 5 crystallizes with one CH<sub>2</sub>Cl<sub>2</sub> molecule. However, two Cl atoms in CH<sub>2</sub>Cl<sub>2</sub> are disordered in three positions and thus refined with 2/3weight for each Cl atom. The Au-SPh group and the Au-Cl group in 5 are in a staggered conformation. Intramolecular aurophilic interaction is again impossible. In the dimer 1, the phenyl group (C7-C12) of the SPh coordinated to Au2 is almost parallel and in close proximity to one of the phenyl groups (C31-C36) of PPh<sub>3</sub> which is coordinated to Au 1. The finding suggests the formation of an 'intramolecular'  $\pi - \pi$  interaction if we treat the dimer of **1** as a molecule. This type of 'intramolecular'  $\pi - \pi$  interaction is not formed in 2 for a single dimer unit and in 3-5 for a single molecule. Au–P distances in 1 are 2.263(9) and 2.28(1) Å, which are longer than that of similar phosphine gold-thiolate, Au(PPh<sub>3</sub>)(8-qnS) (2.248(7) Å) [40]. Au–P distances in 2 are 2.27(1) and 2.18(2) Å, which are close to that of  $(AuCl)_2(\mu$ -trans-dpen) (2.235(2) Å) [32] and that of [Au<sub>2</sub>(*p*-thiocresol)<sub>2</sub>(1,5-bis(diphenylphosphino)pentane] (2.260(1) Å) [26]. The Au–P distance in **3** is 2.274(8) Å. The Au–P distances in 4 are 2.21(1) Å (trans to SPh) and 2.27(1) Å (trans to Cl). These distances in 5 are 2.26(1) (trans to SPh) and 2.25(1) Å (trans to Cl). Au-S distances are 2.30(1) and 2.32(1) in 1, 2.24(3) and 2.33(2) in 2, 2.316(9) in 3, 2.23(1) in 4, and 2.28(2) Å in 5, respectively. These distances are close to that of Au(PPh<sub>3</sub>)(8-qnS) (2.296(8)) [40], those of [Au<sub>2</sub>- $(p - \text{thiocresol})_2(1, 4 - \text{bis}(\text{diphenylphosphino})\text{butane}]$ (2.301(2)) and of Au<sub>2</sub>(p-thiocresol)<sub>2</sub>(1,5-bis-(diphenylphosphino)pentane] (2.313(3) Å) [26]. The Au-S distances in quite analogous [8] (1,1')ferrocenophane,  $[Au_2S_2(CH_2)_3](dppfe)$ , are 2.289(4) and 2.295(4) Å [41].

### 3.3. Crystal structure

The drawings of the crystal packing for 1 (Fig. 6), 2 (Fig. 7), and 4 (Fig. 8) exhibit interesting features. The projection of the molecular packing of 1 along the b



Fig. 5. The ORTEP drawing of (AuSPh)(µ-dppfe)(AuCl) (5).



Fig. 6. The projection of the crystal structure of  $Au(PPh_3)(SPh)$  (1) along the *b* axis, which shows a tetramer structure.



Fig. 7. The projection of the crystal packing of  $(AuSPh)_2(\mu$ -transdepen) (2) along the *c* axis, which shows the two-dimensional network.

axis (Fig. 6) shows a dimer of dimer structure which is composed by two kind of weak interactions, aurophilicity and  $\pi-\pi$  interaction between a phenyl group of PPh<sub>3</sub> (Ph61) coordinated to Au<sub>2</sub> and the phenyl group of SPh (Ph71) coordinated to Au<sub>2</sub>. The Ph71 phenyl group of the SPh ligand overlaps with the Ph61 phenyl ring and the closest interatomic distance is 3.22(4) Å among twelve carbon atoms. These distances are good evidence to indicate a  $\pi-\pi$  interaction between these two phenyl groups. This type of oligomer structure has not yet been reported for 1 to the best of our knowledge [30]; Schmidbaur et al. reported also molecular structures of relevant Ph<sub>3</sub>PAu(S-2, 4, 6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (R = Et and/or iPr) compounds. Au…Au interaction, however, was not demonstrated for these compounds [30]. Bulky R groups in these compounds are a deterrent for  $\pi - \pi$  interactions among aromatic rings as in 1 and such a  $\pi - \pi$  interaction seems to be germane to the aurophilicity for  $Ph_3PAu(S-Ar)$  (Ar = an aromatic ring) type compounds. A projection of the molecular packing along the c axis is displayed in Fig. 7, which demonstrates the formation of an infinite chain polymer connecting  $(AuSPh)_2(\mu$ -trans-dpen) units by Au···Au interaction. The gross polymer structure composed from Au-P-C=C-P-Au units is parallel along the b axis. In addition, the neighboring chains are connected with partial  $\pi - \pi$  stacking between the phenyl rings of the SPh groups (S2C31–C36, hatched) which are coordinated to Au2; the closest contact between carbon atoms in these phenyl rings is 3.0(1) Å. In this way, two-dimensional layered structure is composed by aurophilicity and  $\pi - \pi$  interaction. This layered structure of 2 is reflected in its mechanical property; a single crystal of 2 is easily cleaved by applying a slight pressure along the *ab* plane. This type of network structure has not yet been reported for  $(AuCl)_2(\mu$ -trans-dpen) (7) [32] and  $(AuCl)_2(\mu$ -cis-dpen) [42]. The projection of the molecular packing along the b axis for  $(AuSPh)(\mu$ trans-dpen)(AuCl) (4) (Fig. 8) demonstrates the formation of an infinite chain polymer connecting (AuSPh)(*u-trans-dpen*)(AuCl) units by Au. Au interaction (r(Au - Au) = 3.093(2) Å). The gross core structure composed from the Au-P-C=C-P-Au unit is parallel along the *a* axis and thus SPh groups and C1 groups are parallel, respectively, to each other along the *a* axis. The Au…Au distance in 4 is slightly longer than that of 2 (r(Au - Au) = 3.023(2) Å). This finding supports our expectation that the effect of the SPh group on the aurophilicity is stronger than that of Cl as mentioned



Fig. 8. The projection of the crystal packing of  $(AuSPh)(\mu$ -transdpen)(AuCl) (4) along the *b* axis, which shows the one-dimensional infinite structure.

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above. Similar projections of the molecular packing along the a, b or c axes have been made for dppfe derivatives, 3 and 5. However, the closest Au-Au contact is 5.768(3) for 3 and 5.862(3) Å for 5, respectively, which are beyond the regime of the aurophilicity. In addition, there is no close contact between phenyl groups which suggests a  $\pi - \pi$  interaction. Therefore, construction of an infinite structure and/or a multidimensional array is impossible under these conditions. Our initial strategy to construct a multidimensional array and/or an infinite chain structure by use of augmented aurophilicity in substituted Au(I) complexes with SR group(s) has now been demonstrated in 2 and 4 with and without collaboration of weak  $\pi - \pi$  interaction for less bulky diphosphines such as trans-dpen; this kind of infinite structure has been demonstrated previously for  $(AuX)_2(\mu$ -diphos) where X stands for Cl and/or I and diphos is  $Ph_2P(CH_2)_nPPh_2$  (n = 4, 5, 6, 7,and 8) by Balch et al. [43]. Next we are interested in the role of phosphines for making such a suprastructure. From the inspection of the results on the crystal packing for these five thiophenol gold complexes 1-5, it may be envisaged that the bulky diphosphine ligand such as dppfe is detrimental to the formation of a supramolecular array in the solid state. However, we do not allege that bulky diphosphines cannot induce the aurophilicity itself, because Lacruna et al. have successfully synthesized several Au-dppfe complexes such as [S(Au<sub>2</sub>dppfe)] which have intramolecular Au…Au interactions with the aid of the element, S and/or a ligand containing S to force gold atoms to come close [44]. In addition we [45] and Rheingold et al. have successfully synthesized mixed gold-transition metal clusters such as (Au<sub>2</sub>dppfe)Re<sub>2</sub>(CO)<sub>9</sub> and [(Au<sub>2</sub>dppfe)(AuCl)BRhRu<sub>3</sub>-HCp\*(CO)<sub>o</sub>] in which dppfe bridges a covalent gold-gold bond [46]. These examples suggest that a weaker aurophilic interaction than the covalent gold-gold bond, i.e. intermolecular aurophilicity, should be easily induced between molecules with the aid of a collaboration of weak interactions such as hydrogen bonding. This line of study to construct supramolecular arrays by use of dppfe derivatives of Au(I) is under investigation in our laboratory.

# 3.4. NMR study on the ligand exchange reactions in solutions

The *trans*-dpen complexes **2**, **4**, and **7** and the dppfe complexes **3**, **5**, and **6** each exhibit one phosphorus resonance at  $\delta$  35.87, 32.64, 29.48, 32.80, 30.43, and 27.80, respectively, for <sup>31</sup>P{<sup>1</sup>H} NMR spectra in CDCl<sub>3</sub> at 25°C; the peaks of **4** and **5** are slightly broader than the others. The X-ray molecular structure analysis of **4** and **5** indicates that two phosphorus atoms should be in a different magnetic environment. Thus NMR results suggest that some kind of exchange process in solutions

begets one peak for 4 and 5. Appraisal of the resonances for these complexes has shown that the chemical shift of **4** is close to the center of the signals of **2** and **7** and that of 5 to the center of resonances of 3 and 6. We have made NMR measurements for a mixed solution of 2 and 7, and of 3 and 6 with the ratio 1:1, respectively, in CDCl<sub>3</sub>. <sup>1</sup>H NMR measurements for the former combination have shown a pseudo triplet at  $\delta$  7.22 for ethylene protons which coincides with the pseudo triplet of 4 ( $\delta$  7.22) at room temperature and is in agreement with the center of pseudo triplets of 2 ( $\delta$ 7.29) and 7 ( $\delta$  7.15). <sup>31</sup>P{<sup>1</sup>H} NMR measurement of the latter combination has shown a singlet at  $\delta$  30.98, which is quite close to that of 5 (30.43). The mixed solution of 2 and 7 with a 2:1 ratio in CDCl<sub>3</sub> at room temperature yields a triplet at  $\delta$  7.245 which is in good agreement with the calculated value,  $(7.29 \times 2 + 7.15 \times$ 1)/3 = 7.243. These experiments support the idea that complexes 4 and 5 are in equilibrium for ligand exchange and/or scrambling:

# $2ClAuP^{PAuSPh} \rightleftharpoons ClAuP^{PAuCl}$

## $+ PhSAuP \cap PAuSPh$

where  $P \cap P$  is the *trans*-dpen and/or dppfe. In order to get more information on this process two additional experiments have been made, that is, the concentration and the temperature effect on the exchange process. However, no concentration effect has been detected by



Fig. 9. The upfield shift of the  ${}^{31}$ P NMR chemical shift of 5 with lowering the temperature.



Fig. 10. Temperature-dependent <sup>1</sup>H NMR spectra of the cyclopentadienyl protons for 5 in d<sub>8</sub>-THF.

 ${}^{31}P{}^{1}H$  NMR spectroscopy for 4 (1.0 and 20.0 mmol solutions) and for 5 (1.0 and 10.0 mmol solutions) in CDCl<sub>3</sub> at room temperature. In the temperature dependent <sup>31</sup>P NMR measurements, the signals of 4 and 5 are broadened with lowering the temperature from +50 to  $-50^{\circ}$ C in CDCl<sub>3</sub>. However, the peak never splits into a doublet and/or multiplet and no definitive coalescence has been detected within this range of temperature. Although these broadenings support the idea that 4 and 5 are amenable to the ligand scrambling, one plausible question is why the exchange is so rapid even at -50°C. Previous studies by Balch's group [47] and by Lin's group [48] may provide some clue to this question; both groups have demonstrated by <sup>31</sup>P NMR and UV-Vis spectroscopy that some dinuclear Au(I) complexes bridged by diphosphine ligands are associated to some extent through the intermolecular Au-Au interaction (aurophilicity) even in solution. Under our experimental conditions, the change in concentrations for <sup>1</sup>H NMR and <sup>31</sup>P NMR measurements is more than ten times. However, the results from both measurements are consistent and no concentration dependence is observed. We then have suspected that the ligand scrambling proceeds via the exchange of the Cl atom in 4 or 5 with the Cl atom of CDCl<sub>3</sub> or Cl<sup>-</sup> contained as an impurity in the NMR solvent. Therefore, we have done similar temperature dependent <sup>1</sup>H NMR measurements in a nonchlorinated solvent, that is, deuterated THF,  $d_{\rm s}$ -THF with the temperature range from 50°C to  $-100^{\circ}$ C for 5 to explore the solvent effect on the ligand exchange. The <sup>1</sup>H NMR signals due to Cp ring protons are observed at  $\delta$  4.92 and 4.50, respectively, for 2,5-H and 3,4-H protons as sharper multiplets compared to those in CDCl<sub>3</sub> solution at 25°C. The signals are broadened with decreasing the temperature, but do not split even at -100 °C. Thus it is unlikely

that chlorine exchange with that of the solvent or Cl<sup>-</sup> impurities is a key process for such a rapid scrambling. In the X-ray molecular structure section, it has been suggested that a small amount of impurities are cocrystallized and that these impurities are responsible for the rather high *R* values of these compounds. The findings that the process is not affected by the concentration and the exchange is quite rapid even at low temperature suggest that some intramolecular mechanism is operating for **4** and **5**. On the basis of these discussions we suggest at present that a small amount of impurities in the crystals of **4** and **5** in the form of ClAuP<sup>O</sup>PAuSPh/ClAuP<sup>O</sup>PAuCl or ClAuP<sup>O</sup>PAuSPh/PhSAuP<sup>O</sup>PAuSPh, both of which pairs are connected by aurophilicity, initiates the exchange intramolecularly.

Temperature dependent <sup>31</sup>P NMR (in CDCl<sub>3</sub>) and <sup>1</sup>H NMR (in  $d_8$ -THF) measurements on 5 have revealed another peculiar behavior; <sup>31</sup>P NMR signal is shifted to upfield with lowering the temperature from  $\delta$  30.66 at 50°C to 29.75 at  $-50^{\circ}$ C as is shown in Fig. 9 (such an upfield shift is not detected for 4). The <sup>1</sup>H NMR signal due to 2,5-H protons moves significantly to a lower field ( $\delta$  5.05 at  $-100^{\circ}$ C), while that of 3,4-H protons remains at almost the same field ( $\delta$  4.45) (Fig. 10). We have demonstrated in the previous paper that dppfe can take various conformations due to the rotation of the two cyclopentadienyl rings about the Cp-Fe-Cp axis [49]. Because this rotational motion is slowed with lowering the temperature, the difference of the magnetic field which two kind of protons 'feel' should be enhanced with lowering the temperature to shift the 2,5-H signal to a lower-field. The phosphorus nuclei are close to 2,5-H protons. Thus it is apparent that the rotation about the Cp-Fe-Cp axis is the major origin of the change of the magnetic field to which these nuclei are exposed, although the directions of shifts for <sup>31</sup>P NMR signal and <sup>1</sup>H NMR signal with lowering the temperature are opposite. We stand on the aforementioned interpretation at this moment, but understanding of this upfield shift and the mechanism of rapid ligand scrambling are open to future exploration.

### 4. Supporting material

Tables of atomic coordinates, thermal parameters, and bond lengths and angles: Ordering information is given on any current masthead page.

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