# Synthesis, Structure, and Reactions of Binuclear Gold(I) Complexes Containing Two Different Bridging Ligands

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The binuclear cycloaurated compounds  $[Au_2(\mu-C_6H_3-2-PPh_2-n-Me)_2]$  (n = 5, 1a; n = 6, 1b) react with the digold-(I) complexes  $[Au_2(\mu-S_2CN^nBu_2)_2]$  and  $[Au_2(\mu-dppm)_2](PF_6)_2$  to give heterobridged dinuclear complexes  $[Au_2-M_2](PF_6)_2$ 5, 9a; n = 6, 9b), respectively. Complex 5a exists in the solid state as an infinite zigzag chain of dimeric units with intramolecular Au-Au separations of 2.8331(3) and 2.8243(3) Å for independent molecules and intermolecular Au-Au separations of 3.0653(3) and 3.1304(3) Å. Both 5a and 5b undergo oxidative addition with halogens to X = Cl (6a), I (8a); n = 6, X = Cl (6b), Br (7b), I (8b)]. Compound 8a has been shown by X-ray crystallography to contain a gold(III) atom coordinated in a planar array by bidentate, chelating di-n-butyldithiocarbamate, iodide, and the  $\sigma$ -aryl carbon atom, together with a gold(I) atom that is linearly coordinated by the phosphorus atom of the arylphosphine and by iodide. The intramolecular gold-gold distance of 3.2201(3) Å indicates little or no interaction between the metal atoms. In contrast to the behavior of the homobridged complexes 1a and 1b, the heterobridged dithiocarbamate complexes 5a and 5b give structurally similar products on reaction with halogens, irrespective of the position of the ring methyl substituent. Crystal data for  $[Au_2(\mu-C_6H_3-2-PPh_2-5-Me)(\mu-S_2CN^n-1)]$ Bu<sub>2</sub>)] (5a): triclinic, space group  $P\overline{1}$  (No. 2), with a = 11.3398(1), b = 15.9750(2), c = 16.4400(3) Å,  $\alpha =$ 91.0735(9),  $\beta = 109.3130(7)$ ,  $\gamma = 90.7666(8)^\circ$ , V = 2809.47(6) Å<sup>3</sup>, and Z = 4. Crystal data for [IAu<sup>I</sup>( $\mu$ -2-Ph<sub>2</sub>- $PC_{6}H_{3}$ -5-Me)Au<sup>III</sup>[ $\eta^{2}$ - S<sub>2</sub>CN<sup>n</sup>Bu<sub>2</sub>)] (**8a**): triclinic, space group  $P\overline{1}$  (No. 2), with a = 8.6136(2), b = 9.3273, c = 9.327321.1518(4) Å,  $\alpha = 84.008(1)$ ,  $\beta = 84.945(1)$ ,  $\gamma = 75.181(1)^{\circ}$ , V = 1630.54(6) Å<sup>3</sup>, and Z = 2.

### Introduction

A wide variety of binuclear compounds containing two gold-(I) atoms held in close proximity by a pair of bifunctional ligands is known. Examples of such ligands include dtc,<sup>1,2</sup> dppm,<sup>3</sup> (2-pyridyl)dimethylphosphine,<sup>4</sup> methylenethiophosphinate,<sup>5</sup> and phosphorus bis(ylides).<sup>6,7</sup> The digold(I) complexes characteristically undergo oxidative additions with halogens, pseudohalogens, and, in the case of the bis(ylides), alkyl halides to give either metal–metal bonded digold(II) compounds or heterovalent gold(I)–gold(III) compounds; sometimes both can be

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isolated depending on the conditions.<sup>5–14</sup> In contrast to the numerous homobridged dinuclear gold(I) compounds, relatively few heterobridged analogues are known. Ligand combinations include phosphorus bis(ylides) with bis(diphenylphosphino)-methanide [Ph<sub>2</sub>PCHPPh<sub>2</sub>]<sup>-</sup>,<sup>15</sup> dppm,<sup>16</sup> alkylxanthates,<sup>17</sup> pyridine-2-thiolate,<sup>18</sup> phosphoniodithioformate,<sup>19</sup> and dithiocarbamates.<sup>20</sup> Compounds containing the combinations dppe/*i*-mnt,<sup>21</sup> dppm/

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<sup>(2)</sup> Abbreviations: dtc = dithiocarbamate, R<sub>2</sub>NCS<sub>2</sub><sup>-</sup>; dppm = bis-(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane; *i*-mnt = 1,1-dicyanoethylene-2, 2'-dithiolate, S,S'-S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub><sup>2-</sup>.

Table 1. Elemental Analyses and <sup>31</sup>P{<sup>1</sup>H} NMR Data for Heterobridged Gold Complexes<sup>4</sup>

	Anal. [calcd (found)]					
	color	% C	% H	% N	% other	$\delta_{ ext{P}}{}^{b}$
$[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu-S_{2}CN^{n}Bu_{2})]$ (5a)	orange	38.45 (38.08)	4.03 (4.09)	1.60 (1.52)	3.54 (3.14) (P)	38.4 <sup>c</sup>
$[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-6-Me)(\mu-S_{2}CN^{n}Bu_{2})]\cdot CH_{2}Cl_{2}(5b)$	yellow	36.34 (36.53)	3.79 (4.15)	1.46 (1.68)	3.23 (3.09) (P)	39.6 <sup>c</sup>
$[Au^{I,III}_{2}Cl_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu^{2}-S_{2}CN^{n}Bu_{2})]$ (6a)	yellow	35.57 (35.96)	3.73 (3.70)	1.48 (1.59)	6.78 (6.63) (S)	32.5
$[Au^{I,III}_{2}I_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu^{2}-S_{2}CN^{n}Bu_{2})]$ (8a)	brown	29.80 (30.03)	3.13 (3.39)	1.24 (1.54)	22.49 (22.78) (I)	36.7
$[Au^{I,III}_{2}Cl_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-6-Me)(\mu^{2}-S_{2}CN^{n}Bu_{2})](\mathbf{6b})$	pale yellow	35.57 (35.91)	3.73 (3.93)	1.48 (1.58)	7.50 (7.29) (Cl)	32.5
$[Au^{I,III}_{2}Br_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-6-Me)(\mu^{2}-S_{2}CN^{n}Bu_{2})]$ (7b)	brown	32.51 (32.75)	3.41 (3.36)	1.35 (1.39)	15.45 (15.22) (Br)	33.9
$[Au^{I,III}_{2}I_{2}(\mu - C_{6}H_{3} - 2 - PPh_{2} - 6 - Me)(\mu^{2} - S_{2}CN^{n}Bu_{2})]$ (8b)	orange	29.80 (30.14)	3.13 (3.32)	1.24 (1.10)	22.49 (22.39) (I)	36.2
$[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu-dppm)]PF_{6}(\mathbf{9a})$	pale yellow	nm	nm	_	nm	37.5 <sup>d</sup>
$[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-6-Me)(\mu-dppm)]PF_{6}(9b)$	pale vellow	44.09 (43.71)	3.20 (3.27)	_	10.34 (10.74) (P)	37.2 <sup>d</sup>

<sup>*a*</sup> Abbreviations: nm = not measured. <sup>*b*</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 23 °C. <sup>*c*</sup> In CDCl<sub>3</sub> at 23 °C. <sup>*d*</sup>  $\delta$  (*P*,*C*-ligand);  $\delta$  (dppm) 32.3 ( $\delta_A$ ), 32.7 ( $\delta_B$ ),  $J_{AB} = 59$ ,  $J_{AC} = 8$ ,  $J_{BC} = 308$  Hz (**9a**),  $\delta$  (dppm) 32.2 ( $\delta_A$ ), 32.6 ( $\delta_B$ ),  $J_{AB} = 56$ ,  $J_{AC} = 7$ ,  $J_{BC} = 300$  Hz (**9b**).

Scheme 1



*i*-mnt,<sup>22</sup> dppm/dtc,<sup>22</sup> and dppm/1,3-propanedithiolate<sup>23</sup> are also known. These compounds also undergo oxidative addition reactions with halogens to give metal-metal bonded binuclear gold(II) compounds.<sup>16–19</sup> We have shown<sup>24</sup> that the products obtained by oxidative addition of halogens ( $X_2 = Cl_2, Br_2, I_2$ ) to the binuclear cycloaurated complexes  $[Au_2(\mu-C_6H_3-2-PPh_2$ n-Me)<sub>2</sub>] (n = 5, 1a; n = 6, 1b) differ depending on the position of the ring methyl substituent, as outlined in Scheme 1. In both series, the first isolable products are the homobinuclear digold-(II) complexes 2a and 2b. The former isomerize slowly by intramolecular C-C coupling to give digold(I) complexes 3, whereas, in the 6-methyl series, the complexes 2b isomerize rapidly above -20 °C to the heterobinuclear gold(I)–gold(III) complexes 4, which do not undergo subsequent C-C coupling. We wished to find out whether heterobridged digold(I) complexes containing one bridging C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-n-Me ligand and a different bridging ligand, such as dtc or dppm, could be isolated and if their oxidative addition behavior also would depend on the placement of the ring methyl group. The results of this study are reported here.

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### **Experimental Section**

**General Procedures.** Most syntheses were performed under dry argon with the use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable. Solvents were dried by standard procedures, distilled, and stored under nitrogen.

Physical Measurements. The following instruments were used for spectroscopic measurements: Varian XL-200E (1H at 200 MHz, 31P at 80.96 MHz), Varian Gemini 300 (1H at 300 MHz), Bruker Aspect 2000 (<sup>31</sup>P at 80.96 MHz), VG ZAB-2SEQ [high-resolution EI (electron impact) and FAB (fast atom bombardment) mass spectra], Micromass Platform 2 [electrospray (ES) mass spectra], Perkin-Elmer PE 683 (infrared spectra as KBr disks in the range 4000-400 cm<sup>-1</sup>), and Perkin-Elmer FT 1800 (infrared spectra as polyethylene disks in the range 400–150 cm<sup>-1</sup>). The NMR chemical shifts ( $\delta$ ) are given in ppm relative to TMS (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and referenced either to residual solvent signals (<sup>1</sup>H) or externally (<sup>31</sup>P). Coupling constants (J) are given in hertz. Elemental analyses were performed by the Microanalytical Laboratory of the Research School of Chemistry at the Australian National University. Elemental analyses and <sup>31</sup>P NMR chemical shifts are collected in Table 1. Simulation of the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 9a and 9b was carried out with MestRe-C 2.3 NMR processing and simulation software.25

**Starting Materials.** The compounds  $[Au_2(\mu-C_6H_3-2-PPh_2-n-Me)_2]$ (n = 5, 1a; n = 6, 1b),<sup>24</sup>  $[Au_2(\mu-S_2CN^nBu_2)_2]$ ,<sup>1</sup>  $[Au_2(\mu-dppm)_2]Cl_2$ ,<sup>3</sup> and PhICl<sub>2</sub><sup>26</sup> were prepared by literature procedures.

Digold(I) Complexes,  $[Au_2(\mu-C_6H_3-2-PPh_2-n-Me)(\mu-S_2CN^nBu_2)]$ (n = 5, 5a; n = 6, 5b). A solution or suspension of 1a or 1b (214 mg, 0.23 mmol) in dichloromethane (20 mL) was treated with a solution of  $[Au_2(\mu-S_2CN^nBu_2)_2]$  (182 mg, 0.23 mmol) in dichloromethane (5 mL) and stirred for 30 min at room temperature. Concentration of the pale green solution in vacuo and addition of hexane gave air-stable orange (5a) or yellow (5b) solids in yields of 316 mg (80%) and 275 mg (68%), respectively. Crystals of 5a suitable for X-ray diffraction were obtained from dichloromethane/methanol. 5a. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.9 (t, CH<sub>3</sub> of "Bu), 1.3 (sxt, CH<sub>2</sub> of "Bu), 1.8 (qnt, CH<sub>2</sub> of "Bu), 2.3 (s, C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>), 3.9 (q, CH<sub>2</sub> of <sup>*n*</sup>Bu), 6.8–7.7 (m, arom). EI-MS: m/z874 (*M*<sup>+</sup>), 605, 342. IR (KBr disk): 1576 cm<sup>-1</sup> [*v*(C=N)]. **5b**. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.9 (t, CH<sub>3</sub> of "Bu), 1.4 (sxt, CH<sub>2</sub> of "Bu), 1.8 (qnt, CH<sub>2</sub> of <sup>n</sup>Bu), 2.6 (s, C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>), 3.9 (q, CH<sub>2</sub> of <sup>n</sup>Bu), 6.8-7.7 (m, arom). EI-MS: m/z 874 ( $M^+$ ), 676, 605. IR (KBr disk): 1568 cm<sup>-1</sup>  $[\nu(C=N)].$ 

Gold(I)-Gold(III) Complexes, [XAu( $\mu$ -2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>3</sub>-*n*-Me)AuX-( $\eta$ <sup>2</sup>-S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub>)] [n = 5, X = Cl (6a), I (8a); n = 6, X = Cl (6b), Br (7b), I (8b)]. To a solution of 5a or 5b (50 mg, 0.057 mmol) in dichloromethane (10 mL) at -70 °C was added a solution of iodine,

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Table 2. Crystallographic Data for Compounds 5a and 8a

	5a	8a	
chem formula	C <sub>28</sub> H <sub>34</sub> Au <sub>2</sub> NPS <sub>2</sub>	C <sub>28</sub> H <sub>34</sub> Au <sub>2</sub> I <sub>2</sub> NPS <sub>2</sub>	
fw	873.61	1127.42	
space group	<i>P</i> 1 (no. 2)	$P\overline{1}$ (no. 2)	
a (Å)	11.3398(1)	8.6136(2)	
b (Å)	15.9750(2)	9.3273(2)	
<i>c</i> (Å)	16.4400(3)	21.1518(4)	
$\alpha$ (deg)	91.0735(9)	84.008(1)	
$\beta$ (deg)	109.3130(7)	84.945(1)	
$\gamma$ (deg)	90.7666(8)	75.181(1)	
$V(Å^{3)}$	2809.47(6)	1630.54(6)	
$D_{c}(g \text{ cm}^{-3})$	2.065	2.296	
Ζ	4	2	
$\mu ({\rm cm}^{-1})$	106.92	111.08	
$\lambda$ (Å)	0.7107	0.7107	
<i>T</i> (°K)	200(1)	200(1)	
R (obsd data) % <sup><i>a</i></sup>	3.35	2.97	
$[I > 2\sigma(I)]$			
$R_{\rm w}$ (obsd data) % <sup>b</sup>	3.37	3.38	
$[I > 2\sigma(I)]$			

 ${}^{a}R = \sum |F_{0}| - |F_{c}| / \sum |F_{0}|$ .  ${}^{b}R_{w} = [\sum w(|F_{0}| - |F_{c}|)^{2} / \sum wF_{0}^{2}]^{1/2}$ , where  $w = 1/[\sigma^{2}(F_{0})]$ .

bromine, or PhICl<sub>2</sub> (0.06 mmol) in dichloromethane (5 mL), causing a color change to deep red (I<sub>2</sub>) or orange (Br<sub>2</sub>, PhICl<sub>2</sub>). The mixture was stirred at low temperature for 30 min, allowed to warm to room temperature, and stirred for a further 30 min. Hexane was added, and the solutions were evaporated under reduced pressure until the products began to precipitate. The orange or yellow solids were isolated by filtration and washed with hexane. The yields of **6a**, **8a**, and **6b**–**8b** were ca. 70%. Crystals of **8a** suitable for X-ray diffraction were obtained from dichloromethane/methanol. FAB-MS: m/z 979 ( $M^+$ -Cl), 747, 472, 306 (**6a**); 1025 ( $M^+$ -II) (**8a**); 979 ( $M^+$ -Cl), 747, 472, 306 (**6b**); 1025 ( $M^+$ -Br) (**7b**); 1198 ( $M^+$ ), 1071, 943, 747, 471, 275 (**8b**).

**Digold(I) Complexes, [Au<sub>2</sub>(\mu-C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-***n***-Me)(\mu-dppm)]PF<sub>6</sub> (***n* **= 5, 9a;** *n* **= 6, 9b). A solution or suspension of 1a or 1b (50 mg, 0.053 mmol) in dichloromethane (15 mL) was treated with a solution of [Au<sub>2</sub>(\mu-dppm)<sub>2</sub>]Cl<sub>2</sub> (65 mg, 0.053 mmol) in dichloromethane (5 mL). The mixture was either heated to reflux for 1 h (9a) or stirred for 30 min at room temperature (9b). The solution was evaporated to dryness under reduced pressure, and the residue taken up in acetone (5 mL). The product was precipitated in ca. 80% yield by addition of a concentrated solution of NH<sub>4</sub>PF<sub>6</sub> in acetone. 9a. <sup>1</sup>H NMR (CDCl<sub>3</sub>): \delta 2.3 (s, CH<sub>3</sub>), 3.9 (t, sepn = 10 Hz, CH<sub>2</sub>), 6.9–7.7 (m, arom). ES-MS:** *m***/***z* **1053 (***M***<sup>+</sup>). 9b. <sup>1</sup>H NMR (CDCl<sub>3</sub>): \delta 2.7 (s, CH<sub>3</sub>), 4.1 (t, sepn = 10 Hz, CH<sub>2</sub>), 6.9–7.7 (m, arom). ES-MS:** *m***/***z* **1053 (***M***<sup>+</sup>).** 

**X-ray Crystallography.** The crystal and refinement data for complexes **5a** and **8a** are summarized in Table 2. Data reduction was performed according to ref 27. Both structures were solved by heavy-atom Patterson methods,<sup>28</sup> and refined by use of teXsan.<sup>29</sup> In **5a** there are two independent molecules in the asymmetric crystallographic unit, one *n*-butyl group in each unit being disordered. Hydrogen atoms were included at geometrically determined positions, which were periodically recalculated but not refined. Methyl hydrogen atoms were oriented to best-fit peaks in difference electron density maps. The neutral atom scattering factors were taken from ref 30;  $\Delta f'$  and  $\Delta f''$  values and mass attenuation coefficients were taken from ref 31.

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**Figure 1.** Molecular structure of  $[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu-S_{2}CN^{n}-Bu_{2})]$  (**5a**) with atom labeling; ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.

**Table 3.** Selected Bond Distances (Å) and Angles (Deg) in  $[Au^{I}_{2}(\mu-C_{6}H_{3}-2-PPh_{2}-5-Me)(\mu-S_{2}CN^{n}Bu_{2})]$  (**5a**)<sup>*a*</sup>

$Au(1) \cdots Au(2)$ Au(1) - P(1) Au(1) - S(1) Au(2) - C(2)	2.8331(3) 2.264(2) 2.316(2) 2.039(6)	Au(1)····Au(4) Au(2)-S(2) C(20)-N(1)	3.0653(3) 2.338(2) 1.354(7)
$ \begin{array}{l} S(1)-Au(1)-P(1)\\ S(2)-Au(2)-C(2)\\ S(1)-C(20)-S(2)\\ Au(2)-Au(1)-Au(4)\\ Au(1)-Au(2)-S(2)\\ Au(1)-Au(2)-C(20) \end{array} $	178.20(6) 174.6(2) 127.4(4) 166.35(1) 91.06(4) 113.7(2)	$\begin{array}{l} P(1)-C(1)-C(2)\\ Au(1)-S(1)-C(20)\\ Au(1)-P(1)-C(1)\\ Au(1)-Au(2)-Au(3)\\ Au(1)-Au(2)-C(2) \end{array}$	121.5(5) 110.0(2) 113.0(2) 148.33(1) 93.1(2)

<sup>*a*</sup> In the second, independent molecule Au(3)···Au(4) = 2.8243(3), Au(2)···Au(3) = 3.1304(3); other distances and angles are similar to those given in the Table.

## Results

The digold(I) complexes  $[Au_2(\mu-C_6H_3-2-PPh_2-n-Me)_2]$  (n = 5, 1a; n = 6, 1b) react with an equimolar amount of the dtc complex  $[Au_2(\mu - S_2CN^nBu_2)_2]$  in dichloromethane at room temperature to give the heterobridged digold(I) compounds [Au2- $(\mu$ -C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-*n*-Me) $(\mu$ -S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub>)] (*n* = 5, 5**a**; *n* = 6, 5**b**) as orange or yellow solids, respectively, which are stable to air and moisture and show strong luminescence when exposed to UV light (Scheme 2). Their EI-mass spectra show a parent-ion molecular peak, and their <sup>31</sup>P{<sup>1</sup>H} NMR spectra contain the singlet expected for equivalent phosphorus atoms. The molecular structure of 5a determined by single crystal X-ray diffraction is shown in Figure 1; important bond lengths and angles are listed in Table 3. In each molecule, two linearly coordinated gold(I) atoms are bridged by <sup>*n*</sup>Bu<sub>2</sub>dtc and C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-5-Me (P,C). As also observed in the binuclear gold(I)-dtc compounds,<sup>32,33</sup> the molecules pack in the crystal to generate an infinite zigzag chain of gold atoms. The intramolecular Au-Au separations for the two independent molecules in the asymmetric unit, 2.8331(3) and 2.8243(3) Å, are similar to those in  $[Au_2(\mu-2-C_6H_4PPh_2)_2]$  [2.8594(3) Å]<sup>34</sup> and  $[Au_2(\mu-C_6H_3-2-$ 

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Scheme 2



PPh<sub>2</sub>-6-Me)<sub>2</sub>] [2.861(2) Å],<sup>24</sup> and are significantly greater than those in [Au<sub>2</sub>( $\mu$ -S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>] [2.76,<sup>32</sup> 2.782(1) Å<sup>33</sup> for R = <sup>*n*</sup>Pr, Et, respectively]. Evidently, the intramolecular Au–Au distance in **5a** is dictated mainly by the less compact *P*,*C* bridging ligand. The intermolecular Au–Au separations, 3.0653(3) and 3.1304-(3) Å, are slightly greater than those in [Au<sub>2</sub>( $\mu$ -S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] [3.004(1) Å] but much less than those in [Au<sub>2</sub>( $\mu$ -S<sub>2</sub>CN<sup>*n*</sup>Pr<sub>2</sub>)<sub>2</sub>] (3.40 Å).<sup>32</sup>

Treatment of **5a** or **5b** with 1 mole equiv of PhICl<sub>2</sub>, Br<sub>2</sub>, or I<sub>2</sub> in dichloromethane at -70 °C gives deep orange or red solutions, which fade on warming to room temperature, and from which yellow or orange adducts of empirical formula [Au<sub>2</sub>X<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-*n*-Me)(S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub>)] [*n* = 5, X = Cl (**6a**), I (**8a**); *n* = 6, X = Cl (**6b**), Br (**7b**), I (**8b**)] can be isolated by addition of hexane (Scheme 3). These compounds show singlet  ${}^{31}P{}^{1}H{}$  NMR resonances, the shieldings (Table 1) of corresponding compounds in the 5- and 6-methyl series being very similar and decreasing in the order I > Br > Cl. With the exception of **8b**, the mass spectra do not show a parent ion peak; the highest mass peak generally corresponds to the loss of one halide ion.

An X-ray diffraction study has shown that 8a is a heterovalent gold(I)-gold(III) complex, and the similarity of their spectroscopic properties indicates that 6a, 6b, 7b, and 8b have comparable structures. The molecular structure of 8a is shown in Figure 2, together with atom numbering; selected bond lengths and angles are listed in Table 4. The trivalent gold atom, Au-(2), is coordinated in a planar array by a bidentate, chelate  $S_{2}$ - $CN^{n}Bu_{2}$  group, the carbon atom of a bridging  $C_{6}H_{3}$ -2-PPh<sub>2</sub>-5-Me group, and iodide; the iodide is cis to the  $\sigma$ -bonded carbon atom. The univalent gold atom, Au(1), is coordinated linearly by iodide and the phosphorus atom of the bridging  $C_6H_3$ -2-PPh<sub>2</sub>-5-Me group. The separation between the gold atoms, 3.2201(3) Å, suggests that they interact only weakly, if at all. The Au(III)-S distance trans to iodide, 2.337(2) Å, is close to that observed in  $[Au^{III}(\eta^2 - S_2 CN^n Bu_2)_2][Au^I Br_2], [2.332(9) Å]^{35}$ whereas that trans to the  $\sigma$ -bonded carbon, 2.388(2) Å, is significantly greater, as expected on the basis of trans influence considerations. The asymmetrical binding of the  $\eta^2$ -S<sub>2</sub>CN<sup>n</sup>Bu<sub>2</sub>



**Figure 2.** Molecular structure of  $[Au^{I,III}_2I_2(\mu-C_6H_3-2-PPh_2-5-Me)(\mu^2-S_2CN^nBu_2)]$  (**8a**) with atom labeling; ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.

**Table 4.** Selected Bond Distances (Å) and Angles (Deg) in  $[Au^{I,III}_{2}I_2(\mu-C_6H_3-2-PPh_2-5-Me)(\mu^2-S_2CN^nBu_2)]$  (8a)

•			
Au(1)····Au(2)	3.2201(3)	Au(2) - S(1)	2.337(2)
Au(1) - P(1)	2.256(2)	Au(2) - S(2)	2.388(2)
Au(1) - I(1)	2.5663(5)	Au(2)-I(2)	2.6015(5)
Au(2)-C(2)	2.049(6)	C(20) - N(1)	1.323(8)
C(20) - S(1)	1.728(7)	C(20)-S(2)	1.711(7)
P(1)-Au(I)-I(1)	173.01(4)	C(2)-Au(2)-I(2)	93.2(2)
S(1) - Au(2) - S(2)	74.85(6)	Au(1) - P(1) - C(1)	115.3(2)
S(1)-C(20)-S(2)	113.3(4)	P(1)-C(1)-C(2)	121.4(4)

group in **8a** may be responsible for the slightly larger S–C–S angle of 113° in this compound compared with that in [Au<sup>III</sup>( $\eta^2$ -S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub>)<sub>2</sub>][Au<sup>I</sup>Br<sub>2</sub>] (109°). The angle subtended at Au(2) by the four membered S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub> group (75°) is similar to that in [Au<sup>III</sup>( $\eta^2$ -S<sub>2</sub>CN<sup>*n*</sup>Bu<sub>2</sub>)<sub>2</sub>][Au<sup>I</sup>Br<sub>2</sub>] and in complexes of the same ligand with copper(III)<sup>36</sup> and nickel(II).<sup>37</sup> Other bond lengths and angles are unexceptional.

The far IR spectra of **6a** and **6b** each show a strong band in the region of 330 cm<sup>-1</sup> assignable to  $\nu$ (Au<sup>I</sup>-Cl); the corresponding  $\nu$ (Au<sup>I</sup>-Br) band in the spectrum of **7b** is observed at 234 cm<sup>-1</sup>. Bands at similar positions are found in the spectra of tertiary phosphine–gold(I) complexes.<sup>38–40</sup> The band due to  $\nu$ (Au<sup>III</sup>–Cl) in the spectrum of complexes **6a** and **6b** could not be located.

Reaction of **1a** or **1b** with  $[Au_2(\mu \text{-dppm})_2]Cl_2$  and subsequent addition of NH<sub>4</sub>PF<sub>6</sub> gives the ionic, heterobridged digold(I) complexes  $[Au_2(\mu\text{-}C_6\text{H}_3\text{-}2\text{-PPh}_2\text{-}n\text{-Me})(\mu\text{-dppm})]PF_6$  (n = 5, **9a**; n = 6, **9b**) (Scheme 4). From the <sup>31</sup>P{<sup>1</sup>H} NMR spectra it is apparent that the PF<sub>6</sub><sup>-</sup> counterion forces the equilibrium to the right by selectively precipitating the heterobridged cation. The electrospray mass spectra of **9a** and **9b** show molecular peaks for both cation and anion. The <sup>1</sup>H NMR spectra show a triplet (separation 10 Hz) for the methylene protons and a singlet for

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**Figure 3.** Observed (top) and simulated (bottom)  ${}^{31}P{}^{1}H$  NMR spectrum of **9a**, where  $\delta_A$  32.3,  $\delta_B$  32.7,  $\delta_C$  37.5,  $J_{AB} = 59$ ,  $J_{AC} = 8$ , and  $J_{BC} = 308$  Hz.

Scheme 4



the methyl protons, in the expected ratio of 2:3, in addition to the aromatic protons. The clearest evidence for the heterobridged formulation comes from the <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which display essentially two AB patterns with an additional, much smaller coupling, as illustrated in Figure 3 for complex 9a. The spectrum can be simulated to give the coupling constants  $J_{AB} = 59$  Hz,  $J_{AC} = 8$  Hz, and  $J_{BC} = 308$  Hz, the nuclei being labeled as shown in Scheme 4. The corresponding values for **9b** are:  $J_{AB} = 56$  Hz,  $J_{AC} = 7$  Hz, and  $J_{BC} = 300$  Hz. The magnitude of  $J_{BC}$  is similar to that found in dinuclear gold(I) complexes of the type  $[Au_2X_2L_2]$  [L = Ph<sub>2</sub>PCH<sub>2</sub>CHEtOPPh<sub>2</sub>], for which values of 346 and 338 Hz have been reported, depending on the anionic ligand (X) present.<sup>41</sup> In addition,  $J_{\rm BC}$ is also similar in magnitude to the P-P coupling constants observed for mutually trans tertiary phosphines in planar d<sup>8</sup> and octahedral d<sup>6</sup> complexes of the later transition metals.<sup>42</sup> The coupling constant of 59 Hz between the inequivalent phosphorus atoms of  $\mu$ -dppm is similar in magnitude to those derived from the spectra of diplatinum(I) complexes  $[Pt_2X_2(\mu-dppm)_2]$  (X = Cl, Br, I) and their derivatives.<sup>43–45</sup> Attempts to obtain X-ray quality crystals of 9a or 9b have been unsuccessful so far. In efforts to obtain other heterobridged digold(I) complexes containing  $\mu$ -C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-*n*-Me (n = 5, 6), we either recovered starting materials (in the case of  $[Au_2(\mu-S_2CPEt_3)_2]$ ) or obtained equilibrium mixtures (in the case of  $[Au_2(\mu-i-mnt)_2]$ ).

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Scheme 5



 $\mathsf{R} = \mathsf{CH}_2\mathsf{Ph} \quad \mathsf{i} = \mathsf{Cl}_2, \ \mathsf{Br}_2, \ \mathsf{l}_2 \ ; \ \mathsf{ii} = [\mathsf{Ag}(\mathsf{OClO}_3)(\mathsf{PPh}_3)]$ 

## Discussion

When two homobridged digold(I) complexes are mixed in solution, an equilibrium with the heterobridged species is set up immediately. The latter can be isolated if it is favored by the equilibrium and if it precipitates selectively. Of the systems we have examined with **1a** and **1b**, only di-*n*-butyldithiocarbamate and dppm (in the presence of  $PF_6^-$ ) give isolable heterobridged products.

Addition of halogens to the S<sub>2</sub>CN<sup>n</sup>Bu<sub>2</sub> complexes initially forms very dark solutions that may contain digold(II) intermediates, but these rapidly isomerize to gold(I)-gold(III) isomers, as has also been observed in [Au<sub>2</sub>(µ-S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>].<sup>35,46,47</sup> Complexes 6a, 8a, and 6b-8b represent the first fully characterized examples of heterovalent gold(I)-gold(III) complexes derived from the oxidative addition to heterobridged digold(I) compounds. In contrast to our results, addition of halogens to the heterobridged dibenzyldithiocarbamato bis(ylide) complex 10 gives homobinuclear digold(II) complexes 11, as shown in Scheme 5. These can only be converted into a gold(I)-gold-(III) complex by treatment with [Ag(OClO<sub>3</sub>)(PPh<sub>3</sub>)] to remove the halide, and it was not possible to distinguish between the two structural possibilities, 12a and 12b, for the resulting product.<sup>16</sup> The only general conclusion from these results, considered together, seems to be that coordination of a tertiary phosphine tends to favor the gold(I)-gold(III) arrangement relative to the gold(II)-gold(II) alternative. It is also noteworthy that, in the halogenation of the heterobridged complexes 5a and 5b, isomerization from the presumed digold(II) product (Scheme 3) occurs with equal ease in the 5- and 6-methyl series, in contrast to the behavior of the homobridged complexes 2a and 2b (Scheme 1). Qualitatively, this difference can be ascribed to two factors: (1) the clear preference for the heterobinuclear product induced by dithiocarbamate, except when bis(ylide) is present as co-ligand, and (2) steric destabilization of the digold-(II) homobridged P,C species caused by the presence of two methyl substituents close to the axial halide ligands.

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**Supporting Information Available:** Details of the X-ray structure determinations in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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