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

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The binuclear cycloaurated compounds [$Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2$] ($n = 5$, **1a**; $n = 6$, **1b**) react with the digold(I) complexes [$Au_2(\mu\text{-}S_2CN^nBu_2)_2$] and [$Au_2(\mu\text{-dppm})_2$]$(PF_6)_2$ to give heterobridged dinuclear complexes [$Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)(\mu\text{-}S_2CN^nBu_2)$] ($n = 5$, **5a**; $n = 6$, **5b**) and [$Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)(\mu\text{-dppm})$]$PF_6$, ($n = 5$, **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 give the heterovalent, gold(I)−gold(III) compounds [$XAu^I(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}n\text{-}Me)Au^{III}X(\eta^2\text{-}S_2CN^nBu_2)$] [$n = 5$, 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 σ-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 [$Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(\mu\text{-}S_2CN^nBu_2)$] (**5a**): triclinic, space group $P\bar{1}$ (No. 2), with $a = 11.3398(1)$, $b = 15.9750(2)$, $c = 16.4400(3)$ Å, $\alpha = 91.0735(9)$, $\beta = 109.3130(7)$, $\gamma = 90.7666(8)°$, $V = 2809.47(6)$ Å^3, and $Z = 4$. Crystal data for [$IAu^I(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}5\text{-}Me)Au^{III}I(\eta^2\text{-}S_2CN^nBu_2)$] (**8a**): triclinic, space group $P\bar{1}$ (No. 2), with $a = 8.6136(2)$, $b = 9.3273$, $c = 21.1518(4)$ Å, $\alpha = 84.008(1)$, $\beta = 84.945(1)$, $\gamma = 75.181(1)°$, $V = 1630.54(6)$ Å^3, 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,[1,2] dppm,[3] (2-pyridyl)dimethylphosphine,[4] methylenethiophosphinate,[5] and phosphorus bis(ylides).[6,7] 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 isolated depending on the conditions.[5−14] 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 [$Ph_2PCHPPh_2$]$^-$,[15] dppm,[16] alkylxanthates,[17] pyridine-2-thiolate,[18] phosphoniodithioformate,[19] and dithiocarbamates.[20] Compounds containing the combinations dppe/*i*-mnt,[21] dppm/

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[2] Abbreviations: dtc = dithiocarbamate, $R_2NCS_2^-$; dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane; *i*-mnt = 1,1-dicyanoethylene-2, 2′-dithiolate, *S,S′*−$S_2C_2(CN)_2^{2-}$.

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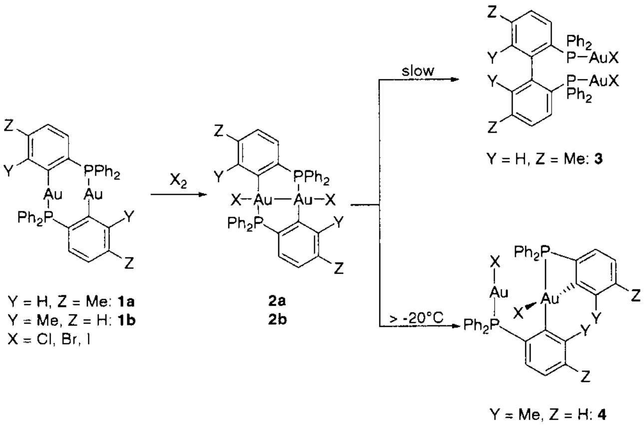
Table 1. Elemental Analyses and $^{31}P\{^1H\}$ NMR Data for Heterobridged Gold Complexes[a]

	Anal. [calcd (found)]					
	color	% C	% H	% N	% other	δ_P[b]
$[Au^I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(\mu\text{-}S_2CN^nBu_2)]$ (**5a**)	orange	38.45 (38.08)	4.03 (4.09)	1.60 (1.52)	3.54 (3.14) (P)	38.4[c]
$[Au^I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)(\mu\text{-}S_2C\,N^nBu_2)]\cdot CH_2Cl_2$ (**5b**)	yellow	36.34 (36.53)	3.79 (4.15)	1.46 (1.68)	3.23 (3.09) (P)	39.6[c]
$[Au^{I,III}_2Cl_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(\mu^2\text{-}S_2CN^nBu_2)]$ (**6a**)	yellow	35.57 (35.96)	3.73 (3.70)	1.48 (1.59)	6.78 (6.63) (S)	32.5
$[Au^{I,III}_2I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(\mu^2\text{-}S_2CN^nBu_2)]$ (**8a**)	brown	29.80 (30.03)	3.13 (3.39)	1.24 (1.54)	22.49 (22.78) (I)	36.7
$[Au^{I,III}_2Cl_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)(\mu^2\text{-}S_2CN^nBu_2)]$ (**6b**)	pale yellow	35.57 (35.91)	3.73 (3.93)	1.48 (1.58)	7.50 (7.29) (Cl)	32.5
$[Au^{I,III}_2Br_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)(\mu^2\text{-}S_2CN^nBu_2)]$ (**7b**)	brown	32.51 (32.75)	3.41 (3.36)	1.35 (1.39)	15.45 (15.22) (Br)	33.9
$[Au^{I,III}_2I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)(\mu^2\text{-}S_2CN^nBu_2)]$ (**8b**)	orange	29.80 (30.14)	3.13 (3.32)	1.24 (1.10)	22.49 (22.39) (I)	36.2
$[Au^I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(\mu\text{-}dppm)]PF_6$ (**9a**)	pale yellow	nm	nm	–	nm	37.5[d]
$[Au^I_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)(\mu\text{-}dppm)]PF_6$ (**9b**)	pale yellow	44.09 (43.71)	3.20 (3.27)	–	10.34 (10.74) (P)	37.2[d]

[a] Abbreviations: nm = not measured. [b] In CD_2Cl_2 at 23 °C. [c] In $CDCl_3$ at 23 °C. [d] δ (*P,C*-ligand); δ (dppm) 32.3 (δ_A), 32.7 (δ_B), $J_{AB} = 59$, $J_{AC} = 8$, $J_{BC} = 308$ Hz (**9a**), δ (dppm) 32.2 (δ_A), 32.6 (δ_B), $J_{AB} = 56$, $J_{AC} = 7$, $J_{BC} = 300$ Hz (**9b**).

Scheme 1



i-mnt,[22] dppm/dtc,[22] and dppm/1,3-propanedithiolate[23] are also known. These compounds also undergo oxidative addition reactions with halogens to give metal–metal bonded binuclear gold(II) compounds.[16–19] We have shown[24] that the products obtained by oxidative addition of halogens ($X_2 = Cl_2, Br_2, I_2$) to the binuclear cycloaurated complexes $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2]$ ($n = 5$, **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 $C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me$ 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.

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, ^{31}P at 80.96 MHz), Varian Gemini 300 (^1H at 300 MHz), Bruker Aspect 2000 (^{31}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^{-1}), and Perkin–Elmer FT 1800 (infrared spectra as polyethylene disks in the range 400–150 cm^{-1}). The NMR chemical shifts (δ) are given in ppm relative to TMS (^1H) and 85% H_3PO_4 (^{31}P) and referenced either to residual solvent signals (^1H) or externally (^{31}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 ^{31}P NMR chemical shifts are collected in Table 1. Simulation of the $^{31}P\{^1H\}$ NMR spectra of **9a** and **9b** was carried out with MestRe-C 2.3 NMR processing and simulation software.[25]

Starting Materials. The compounds $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2]$ ($n = 5$, **1a**; $n = 6$, **1b**),[24] $[Au_2(\mu\text{-}S_2CN^nBu_2)_2]$,[1] $[Au_2(\mu\text{-}dppm)_2]Cl_2$,[3] and $PhICl_2$[26] were prepared by literature procedures.

Digold(I) Complexes, $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)(\mu\text{-}S_2CN^nBu_2)]$ ($n = 5$, 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 $[Au_2(\mu\text{-}S_2CN^nBu_2)_2]$ (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**. ^1H NMR ($CDCl_3$): δ 0.9 (t, CH_3 of ^nBu), 1.3 (sxt, CH_2 of ^nBu), 1.8 (qnt, CH_2 of ^nBu), 2.3 (s, $C_6H_3CH_3$), 3.9 (q, CH_2 of ^nBu), 6.8–7.7 (m, arom). EI-MS: *m/z* 874 (M^+), 605, 342. IR (KBr disk): 1576 cm^{-1} [ν(C=N)]. **5b**. ^1H NMR ($CDCl_3$): δ 0.9 (t, CH_3 of ^nBu), 1.4 (sxt, CH_2 of ^nBu), 1.8 (qnt, CH_2 of ^nBu), 2.6 (s, $C_6H_3CH_3$), 3.9 (q, CH_2 of ^nBu), 6.8–7.7 (m, arom). EI-MS: *m/z* 874 (M^+), 676, 605. IR (KBr disk): 1568 cm^{-1} [ν(C=N)].

Gold(I)–Gold(III) Complexes, $[XAu(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}n\text{-}Me)AuX(\eta^2\text{-}S_2CN^nBu_2)]$ [$n = 5$, 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	$C_{28}H_{34}Au_2NPS_2$	$C_{28}H_{34}Au_2I_2NPS_2$
fw	873.61	1127.42
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	11.3398(1)	8.6136(2)
b (Å)	15.9750(2)	9.3273(2)
c (Å)	16.4400(3)	21.1518(4)
α (deg)	91.0735(9)	84.008(1)
β (deg)	109.3130(7)	84.945(1)
γ (deg)	90.7666(8)	75.181(1)
V (Å$^{3)}$	2809.47(6)	1630.54(6)
D_c (g cm^{-3})	2.065	2.296
Z	4	2
μ (cm^{-1})	106.92	111.08
λ (Å)	0.7107	0.7107
T (°K)	200(1)	200(1)
R (obsd data) %[a] $[I > 2\sigma(I)]$	3.35	2.97
R_w (obsd data) %[b] $[I > 2\sigma(I)]$	3.37	3.38

[a] $R = \Sigma|F_0| - |F_c|/\Sigma|F_0|$. [b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2}$, where $w = 1/[\sigma^2(F_0)]$.

bromine, or $PhICl_2$ (0.06 mmol) in dichloromethane (5 mL), causing a color change to deep red (I_2) or orange (Br_2, $PhICl_2$). 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^+-I) (**8a**); 979 (M^+-Cl), 747, 472, 306 (**6b**); 1025 (M^+-Br) (**7b**); 1198 (M^+), 1071, 943, 747, 471, 275 (**8b**).

Digold(I) Complexes, [Au$_2$(μ-C$_6$H$_3$-2-PPh$_2$-*n*-Me)(μ-dppm)]PF$_6$ (*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 $[Au_2(\mu\text{-dppm})_2]Cl_2$ (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_4PF_6 in acetone. **9a**. ^{1}H NMR ($CDCl_3$): δ 2.3 (s, CH_3), 3.9 (t, sepn = 10 Hz, CH_2), 6.9−7.7 (m, arom). ES-MS: *m*/*z* 1053 (M^+). **9b**. ^{1}H NMR ($CDCl_3$): δ 2.7 (s, CH_3), 4.1 (t, sepn = 10 Hz, CH_2), 6.9−7.7 (m, arom). ES-MS: *m*/*z* 1053 (M^+).

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,[28] and refined by use of teXsan.[29] 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.

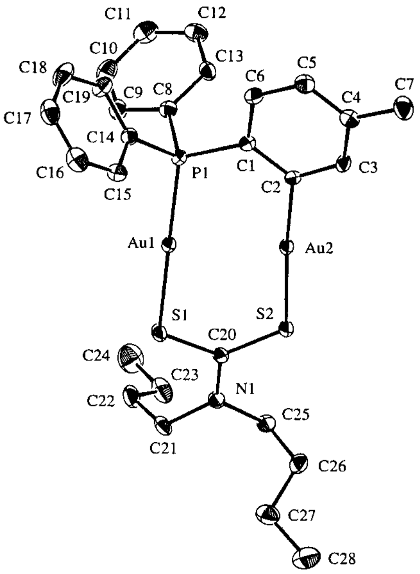

Figure 1. Molecular structure of [Au$^{I}_2$(μ-C$_6$H$_3$-2-PPh$_2$-5-Me)(μ-S$_2$CN^n-Bu$_2$)] (**5a**) with atom labeling; ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (Deg) in [Au$^{I}_2$(μ-C$_6$H$_3$-2-PPh$_2$-5-Me)(μ-S$_2$CN^{n}Bu$_2$)] (**5a**)[a]

Au(1)···Au(2)	2.8331(3)	Au(1)···Au(4)	3.0653(3)
Au(1)−P(1)	2.264(2)	Au(2)−S(2)	2.338(2)
Au(1)−S(1)	2.316(2)	C(20)−N(1)	1.354(7)
Au(2)−C(2)	2.039(6)		
S(1)−Au(1)−P(1)	178.20(6)	P(1)−C(1)−C(2)	121.5(5)
S(2)−Au(2)−C(2)	174.6(2)	Au(1)−S(1)−C(20)	110.0(2)
S(1)−C(20)-S(2)	127.4(4)	Au(1)−P(1)−C(1)	113.0(2)
Au(2)−Au(1)−Au(4)	166.35(1)	Au(1)−Au(2)−Au(3)	148.33(1)
Au(1)−Au(2)−S(2)	91.06(4)	Au(1)−Au(2)−C(2)	93.1(2)
Au(1)−Au(2)−C(20)	113.7(2)		

[a] 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$_2$(μ-C$_6$H$_3$-2-PPh$_2$-*n*-Me)$_2$] (*n* = 5, **1a**; *n* = 6, **1b**) react with an equimolar amount of the dtc complex [Au$_2$(μ-S$_2$CN^{n}Bu$_2$)$_2$] in dichloromethane at room temperature to give the heterobridged digold(I) compounds [Au$_2$(μ-C$_6$H$_3$-2-PPh$_2$-*n*-Me)(μ-S$_2$CN^{n}Bu$_2$)] (*n* = 5, **5a**; *n* = 6, **5b**) 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 ^{31}P{^{1}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 ^{n}Bu$_2$dtc and C$_6$H$_3$-2-PPh$_2$-5-Me (*P*,*C*). As also observed in the binuclear gold(I)−dtc compounds,[32,33] 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$_2$(μ-2-C$_6$H$_4$PPh$_2$)$_2$] [2.8594(3) Å][34] and [Au$_2$(μ-C$_6$H$_3$-2-

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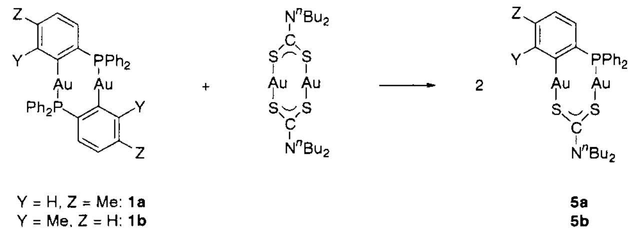
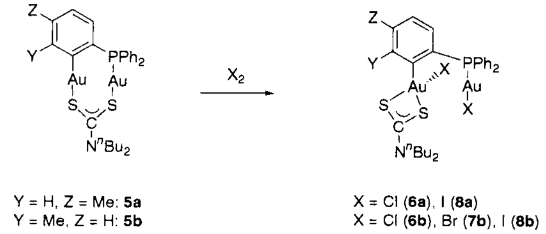
Scheme 2



Scheme 3



PPh$_2$-6-Me)$_2$] [2.861(2) Å],[24] and are significantly greater than those in [Au$_2$(μ-S$_2$CNR$_2$)$_2$] [2.76,[32] 2.782(1) Å[33] for R = ^{n}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$_2$(μ-S$_2$CNEt$_2$)$_2$] [3.004(1) Å] but much less than those in [Au$_2$(μ-S$_2$CN^{n}Pr$_2$)$_2$] (3.40 Å).[32]

Treatment of **5a** or **5b** with 1 mole equiv of PhICl$_2$, Br$_2$, or I$_2$ 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$_2$X$_2$(C$_6$H$_3$-2-PPh$_2$-*n*-Me)(S$_2$CN^{n}Bu$_2$)] [*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$_2$-5-Me group, and iodide; the iodide is cis to the σ-bonded carbon atom. The univalent gold atom, Au(1), is coordinated linearly by iodide and the phosphorus atom of the bridging C$_6$H$_3$-2-PPh$_2$-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}(η^2-S$_2$CN^{n}Bu$_2$)$_2$][Au^{I}Br$_2$], [2.332(9) Å],[35] whereas that trans to the σ-bonded carbon, 2.388(2) Å, is significantly greater, as expected on the basis of trans influence considerations. The asymmetrical binding of the η^2-S$_2$CN^{n}Bu$_2$ group in **8a** may be responsible for the slightly larger S−C−S angle of 113° in this compound compared with that in [Au^{III}(η^2-S$_2$CN^{n}Bu$_2$)$_2$][Au^{I}Br$_2$] (109°). The angle subtended at Au(2) by the four membered S$_2$CN^{n}Bu$_2$ group (75°) is similar to that in [Au^{III}(η^2-S$_2$CN^{n}Bu$_2$)$_2$][Au^{I}Br$_2$] and in complexes of the same ligand with copper(III)[36] and nickel(II).[37] Other bond lengths and angles are unexceptional.

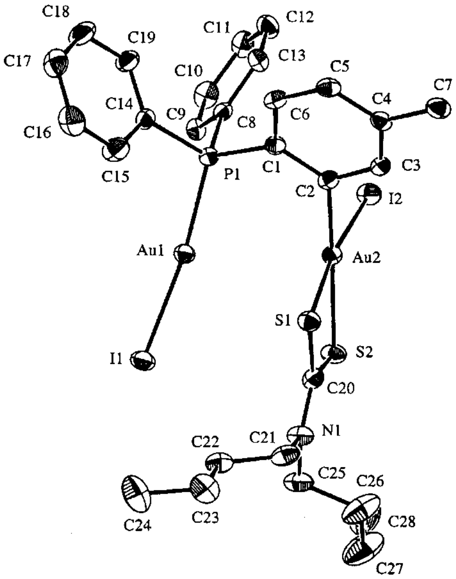


Figure 2. Molecular structure of [Au$^{I,III}{}_2$I$_2$(μ-C$_6$H$_3$-2-PPh$_2$-5-Me)(μ^2-S$_2$CN^{n}Bu$_2$)] (**8a**) with atom labeling; ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (Deg) in [Au$^{I,III}{}_2$I$_2$(μ-C$_6$H$_3$-2-PPh$_2$-5-Me)(μ^2-S$_2$CN^{n}Bu$_2$)] (**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)

The far IR spectra of **6a** and **6b** each show a strong band in the region of 330 cm^{-1} assignable to ν(Au^I-Cl); the corresponding ν(Au^I-Br) band in the spectrum of **7b** is observed at 234 cm^{-1}. Bands at similar positions are found in the spectra of tertiary phosphine−gold(I) complexes.[38−40] The band due to ν(Au^{III}−Cl) in the spectrum of complexes **6a** and **6b** could not be located.

Reaction of **1a** or **1b** with [Au$_2$(μ-dppm)$_2$]Cl$_2$ and subsequent addition of NH$_4$PF$_6$ gives the ionic, heterobridged digold(I) complexes [Au$_2$(μ-C$_6$H$_3$-2-PPh$_2$-*n*-Me)(μ-dppm)]PF$_6$ (*n* = 5, **9a**; *n* = 6, **9b**) (Scheme 4). From the ^{31}P{^{1}H} NMR spectra it is apparent that the PF$_6^-$ 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 ^{1}H NMR spectra show a triplet (separation 10 Hz) for the methylene protons and a singlet for

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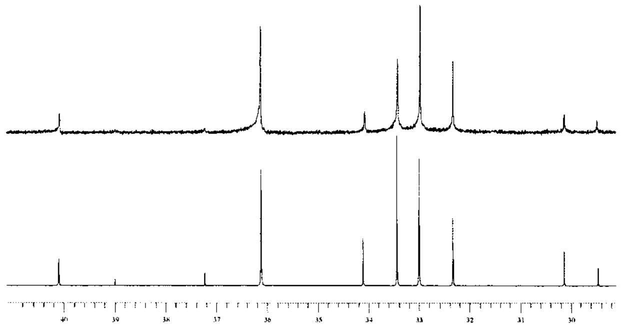
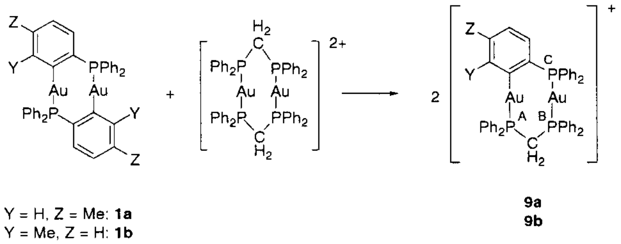


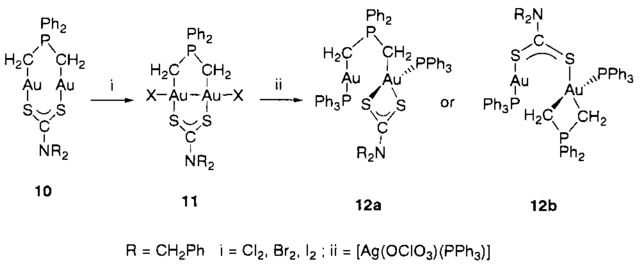
Figure 3. Observed (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of **9a**, where δ_A 32.3, δ_B 32.7, δ_C 37.5, $J_{AB} = 59$, $J_{AC} = 8$, and $J_{BC} = 308$ Hz.

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 $^{31}P\{^{1}H\}$ 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 = $Ph_2PCH_2CHEtOPPh_2$], for which values of 346 and 338 Hz have been reported, depending on the anionic ligand (X) present.[41] In addition, J_{BC} is also similar in magnitude to the P−P coupling constants observed for mutually trans tertiary phosphines in planar d^8 and octahedral d^6 complexes of the later transition metals.[42] The coupling constant of 59 Hz between the inequivalent phosphorus atoms of μ-dppm is similar in magnitude to those derived from the spectra of diplatinum(I) complexes $[Pt_2X_2(\mu\text{-dppm})_2]$ (X = Cl, Br, I) and their derivatives.[43−45] 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 μ-C_6H_3-2-PPh_2-*n*-Me (*n* = 5, 6), we either recovered starting materials (in the case of $[Au_2(\mu\text{-}S_2CPEt_3)_2]$) or obtained equilibrium mixtures (in the case of $[Au_2(\mu\text{-}i\text{-mnt})_2]$).

Scheme 5



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 $S_2CN^nBu_2$ 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 $[Au_2(\mu\text{-}S_2CNEt_2)_2]$.[35,46,47] 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 $[Ag(OClO_3)(PPh_3)]$ to remove the halide, and it was not possible to distinguish between the two structural possibilities, **12a** and **12b**, for the resulting product.[16] 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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