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Notes

Heterobimetallic Complexes of Gold(I) with the Tetrathiovanadate Anion. Crystal Structure of $[VS_4(AuPPh_3)_2\{Au(PPh_3)_2\}]$

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Introduction

The chemistry of the mixed metal−sulfur complexes prepared from tetrathiometalates MS_4^{2-} (M = Mo, W) has been extensively explored because of the potential utility of the anion MoS_4^{2-} in imitation of biological systems, apart from their catalytic applications for hydrodesulfurization and hydrodenitrogenation processes.[1−10] However, VS_4^{3-}, although first prepared in 1890,[11] has been studied only since vanadium nitrogenase was discovered. This molecule is also of interest to inorganic chemists since the coordination chemistry of VS_4^{3-} is still very poorly represented; until now, only some iron[12−14] and copper[15−20] complexes have been prepared.

Here we report on the synthesis and structural characterization of the first heterobimetallic gold(I) complexes with the tetrathiovanadate anion. The crystal structure of $[VS_4(AuPPh_3)_2\{Au(PPh_3)_2\}]$ is described and is shown to be isostructural with the related copper derivative.

Results and Discussion

The reaction of $(NH_4)_3VS_4$ with $[AuCl(PR_3)]$ in dichloromethane gives a dark red solution from which the complexes $[VS_4(AuPR_3)_3]$ (PR_3 = PPh_3 (**1**), PPh_2Me (**2**), PEt_3 (**3**), PMe_3 (**4**), P(*m*-Tol)$_3$ (**5**), P(*p*-Tol)$_3$ (**6**)) can be isolated. Complexes **1**−**6** are dark red solids stable to air and moisture, and they are nonconductors in acetone solutions. Their IR spectra show two absorptions around 440 (s) and 470 (s) cm^{-1} which are typical values for ν(V−S) vibrations. The IR spectrum (KBr) of the starting material $(NH_4)_3VS_4$ presents[14] only one absorption at 478 cm^{-1}; similarly complexes of the type $[VS_4(CuL)_4]^+$ show one strong absorption around 465 cm^{-1}.[20] However, with lower symmetry more absorptions appear.[14−20] The ν(Au−S) absorptions appear around 350 (w) cm^{-1} but in some of the complexes are very weak.

The $^{31}P\{^1H\}$ NMR spectra of complexes **1** and **2** present broad resonances at room temperature, whereas **3**−**6** show sharp singlets. At low temperature all show sharp singlets, which corresponds to a unique phosphorus environment. In the positive liquid secondary ion mass spectra (LSIMS) of complexes **1**−**6** the molecular peaks $[M]^+$ appear at m/z = 1558 (**1**, 22%), 1372 (**2**, 16%), 1125 (**3**, 28%), 999 (**4**, 10%), 1683 (**5**, 6%), and 1683 (**6**, 26%). The association peaks $[M + AuPR_3]^+$ are also present, and in most of the spectra the most intense peak corresponds to the fragment $[S(AuPR_3)_3]^+$.

Crystals of suitable quality for X-ray diffraction could not be grown. Structures may be deduced from the phosphorus chemical shift, which is characteristic of a three-coordinate gold(I) center bonded to one phosphorus and two sulfur atoms. Thus the chemical shift is comparable to that of complexes with the same phosphine ligand such as $[MS_4(AuPR_3)_2]^{21-24}$ or $NBu_4[Au(dmit)(PR_3)]^{25}$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate). For this reason we propose the gold atoms to have a trigonal planar geometry. Two structures containing such a feature are possible 1A or 1B (see Figure 1).

The NMR data suggests structure 1B because in 1A not all of the fragments $AuPR_3^+$ are equivalent and they should give two NMR signals with relative intensity 2:1. However, a clear assignment of the structure to 1B cannot be made because the apparent equivalence of all of the phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectra may arise at a rapid exchange among all $AuPR_3^+$ sites even at low temperature, or because the chemical shifts of both phosphorus environments are so similar that they cannot be distinguished with a 300 MHz NMR spectrophotometer.

The cationic gold complex $[Au(PPh_3)_2](TfO)$ also reacts with $(NH_4)_3[VS_4]$ in dichloromethane, giving a dark red solution from which the compound $[VS_4(AuPPh_3)_2\{Au(PPh_3)_2\}]$ (**7**) can be isolated. The analytical data revealed that **7** has an extra PPh_3 which is bonded to one of the gold atoms, which consequently presents a tetrahedral geometry. According to this, complex **7** can also be prepared by reaction of **1** with triphenylphosphine in a 1:1 molar ratio.

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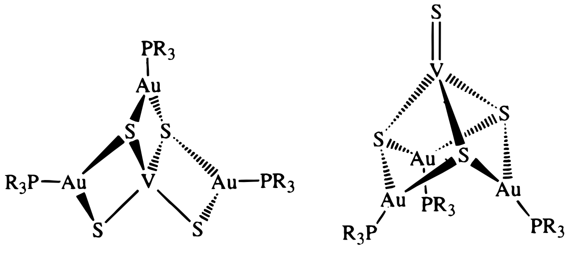

1A 1B

Figure 1. Possible structures (1A or 1B) for complexes **1**−**6**.

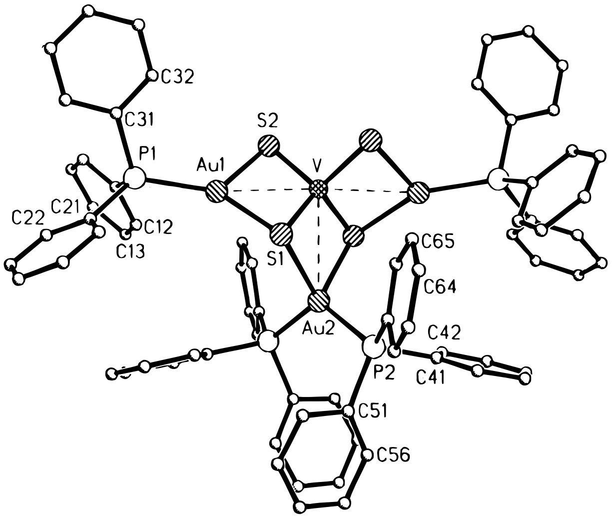

Figure 2. The molecule of complex **7** in the crystal showing the atom-numbering scheme; radii are arbitrary. H atoms are omitted for clarity.

In the IR spectrum of **7** four ν(V−S) stretching modes are manifested at 471 (m), 443 (m), 428 (m), and 416 (m) cm^{-1}, indicating that the irregular atomic arrangement on the periphery of the cluster results in a significant lowering of the symmetry of the VS_4 unit. In the $^{31}P\{^1H\}$ NMR spectrum a broad signal appears at room temperature around 33 ppm. At −55 °C the signal shifts to 42.5 ppm, although is still broad, indicating the existence of rapid equilibrium in solution rendering the phosphines equivalent .

The molecular peak does not appear in the LSIMS+ spectrum of **7**. The most significant peaks are $[VS_4(AuPPh_3)_3]^+$ at *m/z* = 1558, $[VS_4(AuPPh_3)_4]^+$ at *m/z* = 2016, and the fragment $[S(AuPPh_3)_3]^+$ at *m/z* = 1410. However, the molecular weight of **7** in $CHCl_3$ (1795.6) confirms the proposed stoichiometry.

The structure of complex **7** has been established by X-ray diffraction studies. Single crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **7**. The molecule is shown in Figure 2, and selected bond lengths and angles are provided in Table 1. The structure is isostructural to one modification reported for the copper complex $[VS_4(CuPPh_3)_2\{Cu(PPh_3)_2\}]$.[15] The molecule has 2-fold axis symmetry, and consequently only half of it corresponds to the asymmetric unit. There are two different types of gold atoms: one type has tetrahedral geometry, being bonded to two phosphorus and two sulfur atoms, whereas the other type, consisting of two gold atoms, which are equivalent, has a trigonal planar geometry, each gold atom being bonded to one phosphorus and two sulfur atoms. The V−Au distances are 2.8405(7) and 3.034(3) Å; these distances are longer than the V−Cu distances in $[VS_4(CuPPh_3)_2\{Cu(PPh_3)_2\}]$ (2.615(2) and 2.760(8) Å), as expected in changing from a third- to a first-row transition metal, but this probably indicates a weak vanadium−gold interaction. This value is only slightly higher than those found in complexes such as $[V(CO)_3(AuPPh_3)_3]$,[26] in which the Au−V distances range from 2.709 to 2.75 Å, or $[V(CO)_6(AuPPh_3)]$ (2.68 Å),[27] where a metal−metal interaction is proposed.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **7**[a]

Au(1)−P(1)	2.268(3)	Au(1)−S(1)	2.374(3)
Au(1)−S(2)	2.489(3)	Au(1)−V	2.8405(7)
Au(2)−P(2)	2.358(3)	Au(2)−S(1)	2.579(3)
Au(2)−V	3.034(3)	V−S(1)	2.257(3)
V−S(2)	2.142(3)	P(1)−C(11)	1.840(13)
P(1)−C(31)	1.837(12)	P(2)−C(51)	1.805(11)
P(1)−C(21)	1.845(11)	P(2)−C(41)	1.846(11)
P(2)−C(61)	1.818(13)		

P(1)−Au(1)−S(1)	145.66(11)	P(1)−Au(1)−S(2)	117.18(11)
S(1)−Au(1)−S(2)	97.11(9)	P(1)−Au(1)−V	164.00(9)
S(1)−Au(1)−V	50.33(8)	S(2)−Au(1)−V	46.82(8)
P(2)−Au(2)−P(2)#1	121.8(2)	P(2)−Au(2)−S(1)	101.10(10)
P(2)#1−Au(2)−S(1)	118.44(10)	S(1)#1−Au(2)−S(1)	93.10(13)
P(2)−Au(2)−V	119.09(8)	S(1)−Au(2)−V	46.55(6)
S(2)#1−V−S(2)	109.3(2)	S(1)−V−S(1)#1	112.1(2)
S(2)−V−S(1)	111.93(10)	S(1)#1−V−Au(1)#1	54.06(7)
S(2)−V−S(1)#1	105.85(12)	S(2)−V−Au(1)	57.92(8)
S(1)−V−Au(1)#1	123.53(10)	S(1)−V−Au(2)	56.04(9)
S(2)#1−V−Au(1)	124.53(10)	V−S(1)−Au(1)	75.62(10)
S(1)−V−Au(1)	54.06(7)	Au(1)−S(1)−Au(2)	111.33(13)
Au(1)#1−V−Au(1)	176.45(11)	C(31)−P(1)−Au(1)	111.8(3)
S(2)−V−Au(2)	125.37(11)	C(21)−P(1)−Au(1)	117.5(3)
S(1)#1−V−Au(2)	56.04(9)	C(61)−P(2)−Au(2)	117.1(3)
Au(1)−V−Au(2)	88.23(6)		
V−S(1)−Au(2)	77.40(10)		
V−S(2)−Au(1)	75.25(10)		
C(11)−P(1)−Au(1)	112.2(3)		
C(51)−P(2)−Au(2)	108.8(4)		
C(41)−P(2)−Au(2)	117.1(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + ^3/_2$.

Complex **7** contains an essentially tetrahedral VS_4 unit with S−V−S angles ranging from 105.85(12)° to 112.1(2)°. The three gold and vanadium atoms are coplanar. The independent V−S bond lengths are very dissimilar, 2.142(3) and 2.257(3) Å; the shorter is very close to that found in VS_4^{3-} (2.154 Å) and corresponds to the doubly bridging sulfur atoms.

The angles around the trigonal gold atoms are 145.66(11)°, 97.11(9)°, and 117.18(11)°; the main distortion arises at the narrow bite angle of the tetrathiovanadate ligand. The geometry of the other gold center is also distorted mainly because of the S(1)−Au(2)−S(1a) angle of 93.10(13)°. These bite angles are narrower than those found in the copper derivative (101.3(3) and 106.0(2)°) or in the complex $[MoS_4(AuAsPh_3)_2]$ (100.00(9)° and 100.44(9)°).[21] The Au−S distances for the trigonal gold atoms are 2.489(3) and 2.374(3) Å, which are also very dissimilar, although they are of the same order as those in $[MoS_4(AuAsPh_3)_2]$ (2.379(3) and 2.402(3) Å); for the tetrahedral gold center the independent Au−S distance is 2.559(3) Å, which is, as expected, longer than the others but similar to those in other four-coordinate complexes such as $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]$ (2.485(2) and 2.661(2) Å).[28]

As has been mentioned above, the mass spectra of the complexes $[VS_4(AuPR_3)_3]$ present the fragment $[VS_4(AuPR_3)_4]^+$ originated by addition of $AuPR_3^+$ cations to the molecular peak. Thus the cationic species, $[VS_4(AuPR_3)_4]ClO_4$ ($PR_3 = PPh_3$ (**8**),

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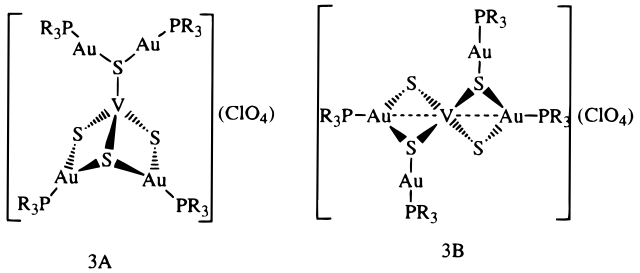

Figure 3. Proposed structures (3A or 3B) for complexes **8** and **9**.

PPh_2Me (**9**)), have been prepared by reaction of $[VS_4(AuPR_3)_3]$ with $[Au(OClO_3)(PR_3)]$ in dichloromethane.

In the IR spectra the absorptions arising at the anion perchlorate appear at 1100 (vs, br) and 620 (m) cm^{-1}; the ν-(V−S) vibrations are present as a broad band at 450 (br, m) and 460 (br, s) cm^{-1} for complexes **8** and **9**, respectively. The $^{31}P\{^1H\}$ NMR spectra at room temperature show two broad signals with similar intensities, which sharpens into two singlets when the experiments are carried out at −55 °C. As the four gold(phosphine) units are not equivalent, these complexes cannot have the same structure as the copper derivatives, $[VS_4(CuL)_4]^{3-}$, in which the VS_4^{3-} anion symmetrically bridges four metallic fragments. The chemical shift indicates that there are two different types of gold atoms, without coupling between them; two of them may have a trigonal planar geometry, and the other two may be linear. Thus two structures are possible (Figure 3, 3A and 3B).

It is proposed that 3A is the most probable structure because it is more similar to that of complex **7**, although it is not possible to discard structure 3B. In the ^1H NMR spectrum of complex **9** a broad signal due to the methyl protons appears; at −55 °C the signal splits into two doublets with equal intensity, which agrees with the proposal of two different phosphine environments. In the LSIMS+ spectra of complexes **8** and **9** the cation molecular peaks appear at $m/z = 2016$ (11%) and 1767 (12%), respectively.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C, H, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$ (unless otherwise stated). Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external).

Materials. The starting material $[Au(PPh_3)_2]TfO$ was prepared from $[AuCl(PPh_3)]$[29] by reaction with $[Ag(TfO)(PPh_3)]$ in dichloromethane and $[Au(OClO_3)PR_3]$ from $[AuCl(PR_3)]$[29] and $AgClO_4$. $(NH_4)_3VS_4$ was commercially available (Strem).

Safety Note. *CAUTION!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Syntheses. $[VS_4(AuPR_3)_3]$ ($PR_3 = PPh_3$ (1), PPh_2Me (2), PEt_3 (3), PMe_3 (4), P(*m*-Tol)$_3$ (5), P(*p*-Tol)$_3$ (6)). To a solution of $[AuCl(PR_3)]$ (0.3 mmol; 0.079 g, PPh_3; 0.06 g, PPh_2Me; 0.036 g, PEt_3; 0.023 g, PMe_3; 0.087 g, P(*m*-Tol)$_3$; 0.087 g, P(*p*-Tol)$_3$) in dichloromethane (20 mL) was added $(NH_4)_3VS_4$ (0.3 mmol, 0.070 g). The suspension was stirred for 2 h, and then the solution was filtered over Celite. Evaporation of the solvent to ca. 5 mL and addition of hexane (15 mL) gave complexes **1**−**6** as red solids. Complex **1**: yield 77%. (Found: C, 41.45; H, 2.52; S, 7.99. Calcd for $C_{54}H_{45}Au_3P_3S_4V$: C, 41.66; H, 2.91; S, 8.24.) IR spectrum (Nujol): 471 (s), 438 (s) cm^{-1} ν(VS). $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 42.2 (s). Complex **2**: yield 73%. (Found: C, 34.17; H, 2.87; S, 9.36. Calcd for $C_{39}H_{39}Au_3P_3S_4V$: C, 34.04; H, 2.49; S, 8.96.) IR spectrum (Nujol): 474 (vs), 459 (vs) cm^{-1} ν(VS); 352 (w) cm^{-1} ν(Au−S). $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 24.8 (s). ^1H NMR ($CDCl_3$ −55 °C): δ 2.28 (d, 9H, PMe, *J*(PH) 9.52 Hz). Complex **3**: yield 80%. (Found: C, 18.86; H, 3.63; S, 11.52. Calcd for $C_{18}H_{45}Au_3P_3S_4V$: C, 19.22; H, 4.03; S, 11.40.) IR spectrum (Nujol): 469 (vs), 443 (vs) cm^{-1} ν(VS); 358 (w) cm^{-1} ν(Au−S). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 −80 °C): δ 38.9 (s). ^1H NMR (CD_2Cl_2): δ 1.25 (m, 27H, PCH_2CH_3), 1.95 (m, 18H, PCH_2CH_3). Complex **4**: yield 75%. (Found: C, 10.83; H, 2.73; S, 12.85. Calcd for $C_9H_{18}Au_3P_3S_4V$: C, 10,75; H, 2.39; S, 12.59.) IR spectrum (Nujol): 473 (vs), 443 (vs) cm^{-1} ν(VS); 352 (w) cm^{-1} ν(Au−S). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 −80 °C): δ −7.4 (s). ^1H NMR (CD_2Cl_2): δ 1.80 (d, 27H, PCH_3, *J*(PH) 10.50 Hz). Complex **5**: yield 89%. (Found: C, 45.18; H, 4.21; S, 6.91. Calcd for $C_{63}H_{63}Au_3P_3S_4V$: C, 44.95; H, 3.77; S, 7.69.) IR spectrum (Nujol): 464 (vs), 439 (sh, m) cm^{-1} ν(VS). $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 43.0 (s). ^1H NMR ($CDCl_3$): δ 2.16 (s, 27H, Me). Complex **6**: yield 89%. (Found: C, 44.62; H, 3.77; S, 7.69. Calcd for $C_{39}H_{39}Au_3P_3S_4V$: C, 44.95; H, 3.77; S, 7.69.) IR spectrum (Nujol): 466 (s), 439 (s) cm^{-1} ν(VS). $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 40.3 (s). ^1H NMR ($CDCl_3$): δ 2.29 (s, 27H, Me).

Table 2. Crystallographic Data for Complex **7**

empirical formula	$C_{72}H_{60}Au_3P_4S_4V$	D_c/g cm^{-3}	1.806
space group	*C*2/*c*	M	1819.16
a/Å	32.110(6)	*T*/°C	−100
b/Å	13.087(2)	λ/Å	0.710 73
c/Å	20.620(3)	μ(Mo *K*α)/cm^{-1}	69.56
β/deg	129.466(7)	R^a (F, $F > 4\sigma(F)$)	0.039
V/Å^3	6689(2)	$R_w{}^b$ (F^2, all reflns)	0.081
Z	4		

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program.

$[VS_4(AuPPh_3)_2\{Au(PPh_3)_2\}]$ (7). Method 1: To a dichloromethane solution (20 mL) of $[VS_4(AuPPh_3)_3]$ (0.1 mmol, 0.156 g) was added PPh_3 (0.1 mmol, 0.026 g), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of diethyl ether (15 mL) gave complex **7** as a red solid. Method 2: To a dichloromethane solution (20 mL) of $[Au(PPh_3)_2](TfO)$ (0.3 mmol, 0.261 g) was added $(NH_4)_3VS_4$ (0.3 mmol, 0.070 g), and the suspension was stirred for 1 h. The solution was filtered over Celite and then concentrated to ca. 5 mL. Addition of diethyl ether (15 mL) afforded a red solid of complex **7**. Yield: 93% and 82%, respectively. (Found: C, 47.58; H, 3.34; S, 6.97. Calcd for $C_{72}H_{60}Au_3P_4S_4V$: C, 47.53; H, 3.32; S, 7.0.5.) $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 42.5 (s).

$[VS_4(AuPR_3)_4](ClO_4)$ ($PR_3 = PPh_3$ (8), PPh_2Me (9)). To a dichloromethane solution (20 mL) of $[VS_4(AuPR_3)_3]$ (0.1 mmol, 0.156 g, PPh_3; 0.137 g, PPh_2Me) was added $[Au(OClO_3)(PR_3)]$ (0.1 mmol; PPh_3, 0.056 g; PPh_2Me, 0.049 g). The mixture was stirred for 10 min, and then evaporation of the solvent to ca. 5 mL and addition of hexane (15 mL) gave complexes **8** and **9** as red solids. Complex **8**: yield 87%. (Found: C, 40.40; H, 2.50; S, 5.98. Calcd for $C_{72}H_{60}Au_4ClO_4P_4S_4V$: C, 40.88; H, 2.86; S, 6.06.) $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 41.7 (s), 32.7 (s). Complex **9**: yield 80%. (Found: C, 33.36; H, 2.67; S, 6.37. Calcd for $C_{52}H_{52}Au_4ClO_4P_4S_4V$: C, 33.45; H, 2.81; S, 6.87.) $^{31}P\{^1H\}$ NMR ($CDCl_3$ −55 °C): δ 24.4 (s), 17.3 (s). ^1H NMR ($CDCl_3$ −55 °C): δ 1.94 (d, 6H, PMe, *J*(PH) 8.61 Hz), 2.30 (d, 6H, PMe, *J*(PH) 8.60 Hz).

Crystal Structure Determinations. The crystal was mounted in inert oil on a glass fiber and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 low-temperature attachment. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å). Scan type: $\theta - 2\theta$. Cell constants were refined from setting angles of ca. 60 reflections in the range 2θ 10−

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(29) Usón, R.; Laguna, A. *Inorg. Synth.* **1982**, *21*, 71.

25°. Absorption corrections were applied on the basis of Ψ-scans. The structure was solved by the heavy-atom method and refined on F^2 using the program SHELXL-93.[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table 2.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, for the structure determination of $[VS_4(AuPPh_3)_2\{Au(PPh_3)_2\}]$ is available on the Internet only. Access information is given on any current masthead page.

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(30) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement;* University of Göttingen: Göttingen, Germany, 1993.