and the National Institutes of Health (Grant HL-13157, J.A.I.). The NMR instrument was funded by the National Science Foundation (Grant CHE81-09064). We thank Prof. B. M. Hoffman for the use of his ESR instrument. We are thankful for Pat Bethel's assistance in obtaining mass spectral data at the Mass Spectrometry Facility, University of California, San Francisco, supported by the NIH Division of Research Resources (Grant RR01614). J.M.G.'s portion of this work is dedicated to his father, James H. Garner.

Registry No. PEt_3, 554-70-1; PMe_3, 594-09-2; Re(OEP)(O)(Cl), 117201-90-8; Re(TPP)(O)(Cl), 117201-86-2; $Re(OEP)(PMe_3)_2$, 117201-87-3; $Re(TPP)(PMe_3)_2{\cdot}C_6H_5CH_3$, 117201-89-5; $Re(OEP)(PEt_3)_2$, 117201-91-9; $Re(TPP)(PEt_3)_2$, 117201-92-0.

Supplementary Material Available: Table SI (crystallographic details), Table SII (anisotropic thermal parameters and hydrogen atom parameters), Table SIV (bond distances and angles), Table SV (least-squares planes and dihedral angles between the least-squares planes) (9 pages); Table SIII (observed and calculated structure amplitudes) (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Cluster Cation $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, Containing both PtAu and PtAg Bonds

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Received April 14, 1988

The chemistry of complexes containing either Pt–Au or Pt–Ag bonds is a rapidly growing area of research.[2-10] The compounds are of interest because of their new and interesting structures and bonding modes and as models for the heterobimetallic metal catalysts. For example, gold leads to significant changes in the catalytic activity and selectivity of platinum catalysts.[11]

Gold has a strong tendency to form Au–Au bonds or bridged AuM_2 or AuM_3 units and most Pt–Au-bonded complexes fall into one of these categories.[2-5] There are well-characterized compounds with simple Au–Pt bonds, but they are ligand bridged.[6] A common synthetic method for introduction of gold–metal bonds is to treat a metal hydride with an LAu^+ derivative, leading to isolobal substitution of LAu^+ for H^+ and hence formation of an Au–M bond. Braunstein synthesized the first PtAu cluster in this way by treating $[PtHCl(PEt_3)_2]$ with 2 equiv of Ph_3PAu^+ to give the cluster cation $[PtCl(AuPPh_3)_2(PEt_3)_2]^+$, but the introduction of only one LAu^+ unit was not achieved.[3]

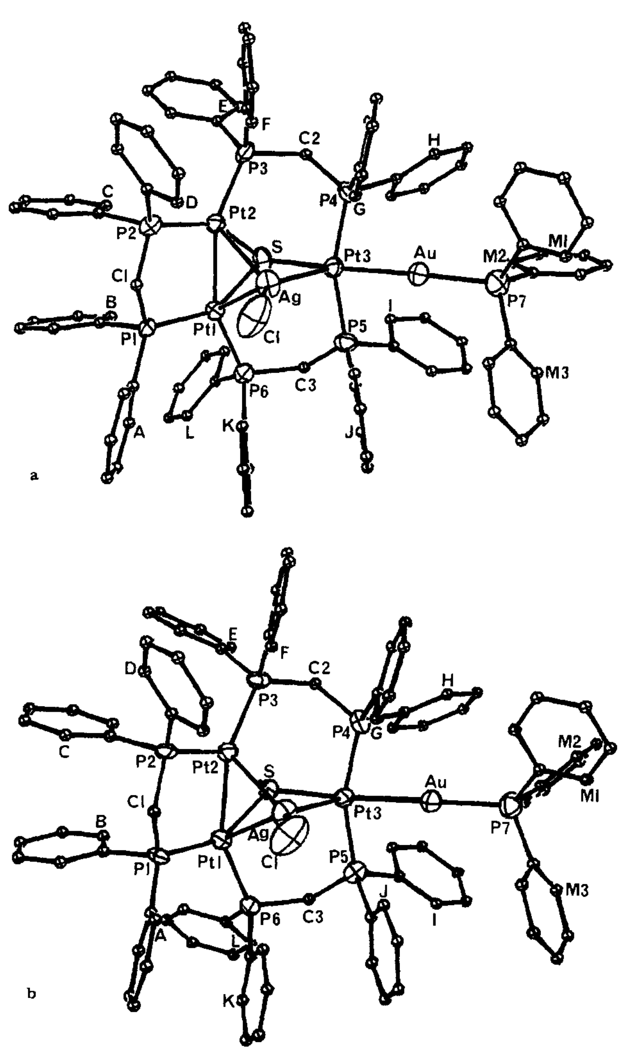

Figure 1. Views of (a) cation A and (b) cation B showing the numbering of the atoms. The carbon atoms of rings A to M3 are numbered cyclically from $n = 1$ to 6, starting with the atom attached to phosphorus. The ring label is placed adjacent to the $n = 2$ atom of each ring. The 50% probability ellipsoids are shown for Au, Pt, Ag, Cl, S, and P atoms. Carbon atoms are represented by spheres of arbitrary size.

As part of our studies of Pt–Au-bonded compounds,[12] reactions of $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}dppm)_3]^+$ (1^+) (dppm = $Ph_2PCH_2PPh_2$)[13] with Ph_3PAu^+ were carried out with the aim of substituting the hydride ligand by the Ph_3PAu unit. The target molecules could not be prepared, but the title complex, containing the Pt_3AuAg core, was isolated instead. This paper reports the synthesis, structure, and spectroscopic properties of this complex.

Results and Discussion

A solution containing $[Au(NO_3)(PPh_3)]$ and a suspension of AgCl was prepared by mixing approximately equimolar amounts of $[AuCl(PPh_3)]$ and $AgNO_3$ in dichloromethane/methanol. Addition of this mixture to $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}dppm)_3]PF_6$ (**1**) in dichloromethane caused an immediate color change from yellow to red, and the product $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}dppm)_3]PF_6$ (**2**) was isolated in good yield. If the AgCl precipitate

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(1) (a) University of Glasgow. (b) University of Western Ontario.
(2) Braunstein, P.; Rose, J. *Gold Bull.* **1985**, *18*, 17.
(3) Braunstein, P.; Lehner, H.; Matt. D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*,
(4) Boyle, P. D.; Johnson, B. J.; Alexander, B. D.; Casalnuovo, J. A.; Gannon, P. R.; Johnson, S. M.; Larka, E. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1987**, *26*, 1346.
(5) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Bosman, W. P.; Behm, H.; Beurskens, P. T.; Steggerda, J. J. *Recl.: J. R. Neth. Chem. Soc.* **1987**, *106*, 157.
(6) Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992.
(7) Usón, R. *Pure Appl. Chem.* **1986**, *58*, 647.
(8) Usón, R.; Fornies, J.; Tomes, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1987**, *26*, 3482.
(9) Bhaduri, S.; Sharma, K.; Jones, P. G.; Erdbrügger, C. F. *J. Organomet. Chem.* **1987**, *326*, C46.
(10) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1986**, 835.
(11) Pruett, R.; Bradley, J. Eur. Pat. 37700, 1982; *Chem. Abstr.* **1982**, *96*, 35540k. Walker, W. E.; Brown, E. S.; Pruett, R. L. U.S. Pat. 3878292, 1975; *Chem. Abstr.* **1975**, *83*, 45426Y. Schwank, J. *Gold Bull.* **1985**, *18*, 1.
(12) Smith, D. E.; Welch, A. J.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4616. Arsenault, G. J.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Treurnicht, I. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 86. Manojlović-Muir, Lj.; Muir, K. W.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 2418.
(13) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1809; *Inorg. Chem.* **1987**, *26*, 3776.

0020-1669/88/1327-4516$01.50/0

Table I. Principal Dimensions of $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$ (**2**)

	cation A	cation B		cation A	cation B
		Distances (Å)			
Au–Pt(3)	2.577 (3)	2.575 (3)	Au–P(7)	2.287 (11)	2.265 (11)
Pt(1)–Pt(2)	2.615 (3)	2.619 (3)	Pt(1)–P(1)	2.249 (10)	2.249 (10)
Pt(1)–Ag	2.808 (4)	2.843 (4)	Pt(2)–P(2)	2.241 (10)	2.261 (10)
Pt(2)–Ag	2.861 (4)	2.832 (4)	Pt(1)–P(6)	2.235 (12)	2.301 (12)
Pt(3)–Ag	2.780 (4)	2.768 (4)	Pt(2)–P(3)	2.284 (10)	2.298 (10)
Pt(1)–S	2.278 (9)	2.278 (9)	Pt(3)–P(4)	2.281 (11)	2.272 (11)
Pt(2)–S	2.257 (11)	2.274 (10)	Pt(3)–P(5)	2.294 (11)	2.254 (12)
Pt(3)–S	2.383 (9)	2.394 (9)	Ag–Cl	2.413 (11)	2.388 (10)
Pt(1)···Pt(3)	3.674 (2)	3.726 (2)	Au···Ag	4.414 (3)	4.361 (3)
Pt(2)···Pt(3)	3.642 (2)	3.631 (2)	P–C mean	1.828 (4)	
Ag···S	3.255 (8)	3.243 (9)	P–C range	1.77 (5)–1.87 (5)	
		Angles (deg)			
Pt(2)–Pt(1)–Ag	63.6 (1)	62.3 (1)	Pt(1)–Pt(2)–Ag	61.5 (1)	62.7 (1)
Pt(2)–Pt(1)–S	54.4 (3)	54.8 (3)	Pt(1)–Pt(2)–S	55.2 (3)	55.0 (3)
Pt(2)–Pt(1)–P(1)	96.7 (3)	96.4 (3)	Pt(1)–Pt(2)–P(2)	94.1 (3)	94.4 (3)
Pt(2)–Pt(1)–P(6)	154.2 (3)	152.7 (3)	Pt(1)–Pt(2)–P(3)	154.5 (3)	154.4 (3)
Ag–Pt(1)–S	78.8 (3)	77.7 (3)	Ag–Pt(2)–S	78.0 (3)	78.0 (3)
Ag–Pt(1)–P(1)	97.1 (3)	94.8 (3)	Ag–Pt(2)–P(2)	92.1 (3)	92.4 (3)
Ag–Pt(1)–P(6)	109.5 (3)	106.7 (3)	Ag–Pt(2)–P(3)	114.1 (3)	114.8 (3)
S–Pt(1)–P(1)	149.8 (4)	150.6 (4)	S–Pt(2)–P(2)	148.8 (4)	149.0 (4)
S–Pt(1)–P(6)	100.5 (4)	99.6 (4)	S–Pt(2)–P(3)	99.6 (4)	99.5 (4)
P(1)–Pt(1)–P(6)	109.0 (4)	109.8 (4)	P(2)–Pt(2)–P(3)	111.4 (4)	111.3 (4)
Au–Pt(3)–Ag	110.9 (1)	109.4 (1)	Ag–Pt(3)–P(4)	101.1 (3)	103.9 (3)
Au–Pt(3)–S	171.3 (3)	172.9 (3)	Ag–Pt(3)–P(5)	94.0 (3)	93.5 (3)
Au–Pt(3)–P(4)	81.7 (3)	81.0 (3)	S–Pt(3)–P(4)	97.0 (4)	95.7 (4)
Au–Pt(3)–P(5)	80.7 (3)	82.4 (3)	S–Pt(3)–P(5)	98.9 (4)	99.3 (4)
Ag–Pt(3)–S	77.7 (3)	77.4 (3)	P(4)–Pt(3)–P(5)	160.0 (4)	159.1 (4)
Pt(1)–Ag–Pt(2)	54.9 (1)	55.0 (1)	Cl–Ag–Pt(1)	122.2 (4)	131.1 (4)
Pt(1)–Ag–Pt(3)	82.2 (1)	83.2 (1)	Cl–Ag–Pt(2)	132.7 (4)	134.1 (4)
Pt(2)–Ag–Pt(3)	80.4 (1)	80.8 (1)	Cl–Ag–Pt(3)	145.5 (4)	139.3 (4)
Pt(3)–S–Pt(1)	104.0 (4)	105.8 (4)	Pt(3)–S–Pt(2)	103.4 (4)	102.1 (4)
Pt(1)–S–Pt(2)	70.4 (3)	70.3 (3)	Pt(3)–Au–P(7)	174.4 (3)	174.1 (3)
P(1)–C(1)–P(2)	113 (2)	115 (2)	P(5)–C(3)–P(6)	120 (2)	122 (2)
P(3)–C(2)–P(4)	118 (2)	120 (2)			

Table II. Crystallographic Data for $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$ (**2**)

$C_{93}H_{81}AgAuClF_6P_8Pt_3S$	fw = 2518.08
a = 17.639 (5) Å	space group: $P\bar{1}$
b = 18.651 (5) Å	T = 22 °C
c = 28.328 (6) Å	λ = 0.71069 Å
α = 94.83 (2)°	ρ_{calcd} = 1.823 g cm^{-3}
β = 98.88 (2)°	μ = 66.5 cm^{-1}
γ = 90.33 (3)°	transmissn coeff = 0.76–1.57
V = 9173 (4) Å^3	$R(F_o)$ = 0.061
Z = 4	$R_w(F_o)$ = 0.0679

was removed before mixing the solutions, a reaction occurred, but the product was too unstable to be isolated.

The structure of complex **2** was determined by X-ray analysis (Figure 1). Crystals of **2** are constructed of well-separated $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]^+$ cations and PF_6^- anions. The presence of four cations and four anions in the centrosymmetric triclinic unit cell implies that two of the cations, designated A and B, are crystallographically independent, as indeed are two of the PF_6^- anions. Cations A and B are chemically identical, and the small structural differences they display can be ascribed to their different environments within the crystal. The most notable of these structural differences are (i) in the orientations of corresponding dppm phenyl rings, particularly ring L, (ii) in the interatomic distances and angles involving the Ag and Cl atoms (see Table I), and (iii) in the conformations and orientations of the PPh_3 ligands. Although a least-squares fit of the two $AuPt_3AgClSP_7C_3$ units yields a rms difference of 0.11 Å between the two sets of atomic positions, with C(1) and P(7) being notably discrepant, corresponding bond lengths and angles in cations A and B agree well, except for those involving the Ag and Cl atoms. In both cations the atoms Pt(3), Ag, and S define an approximate mirror plane; the most obvious distortions from C_s symmetry arise from the orientations of the phenyl ring pairs A,D and E,L and from the conformations adopted by the PPh_3 ligands.

The structure of each cation is based on an approximately isosceles triangle of platinum atoms. Only Pt(1) and Pt(2) are directly bonded to one another. Each edge of the triangle is bridged by a dppm ligand, and opposite faces are capped by μ_3-bridging AgCl and S groups. The cluster is completed by a terminal $AuPPh_3$ fragment attached to Pt(3). The coordination geometries of Pt(1) and Pt(2) are very similar: the phosphorus atoms attached to Pt(1) and Pt(2) lie within 0.40 (1) Å of the Pt(1)Pt(2)S plane, which is roughly normal to the Pt(1)Pt(2)Ag unit [dihedral angles of 95.1 (3) and 94.4 (3)°]. The Pt(3) atom has a distorted square-pyramidal coordination: in A the $AuSP_2$ donor set is planar to within 0.019 (9) Å, whereas in B these four atoms deviate by up to 0.091 (9) Å from their common plane. In both A and B the Pt(3) atom is displaced from the $AuSP_2$ plane toward the capping Ag atom by similar amounts [0.195 (1) and 0.181 (1) Å] and the Pt(3)–Ag bond is bent away from the normal to the $AuSP_2$ plane, giving Ag–Pt(3)–S angles of 77.7 (3) and 77.4 (3)°.

It therefore transpires that cations of **2** are derived from those of **1** by replacement of H^+ by $AuPPh_3^+$ and addition of AgCl to the vacant face of the Pt_3 triangle. Consequent changes in the structural parameters of the $Pt_3(\mu_3\text{-}S)P_6$ molecular skeleton are slight. The mean Pt(1)–Pt(2) bond length in **2** [2.617 (2) Å] is slightly longer than the corresponding distance in **1** [2.597 (4) Å].[13] The nonbonding Pt(1)···Pt(3) and Pt(2)···Pt(3) distances [3.631 (2)–3.726 (2) Å], also longer on average than those in **1** [3.574 (2)–3.678(7) Å], may reflect the steric demand of the additional capping unit. In $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$ (**3**)[14] and $[Pt_3(\mu\text{-}HC{\equiv}CH)Cl(\mu\text{-dppm})_3]^+$ (**4**),[15] which are structurally related to **1**, the nonbonded M···M distances are shorter: 3.508 (1) Å in **3** and 3.232 (2)–3.277 (2) Å in **4**. In **2** the capping S atom is 0.12 Å further from Pt(3) than it is from Pt(1) or Pt(2) [mean Pt–S distances of 2.272 (5) Å for Pt(1) and Pt(2) and 2.389 (6) Å for Pt(3)]. This may indicate that $AuPPh_3$ exerts a high

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(14) Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190.

(15) Douglas, G.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6527.

Table III. Fractional Coordinates and Isotropic Displacement Parameters for $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$ (**2**)

	x/a	*y/b*	*z/c*	U,^{a} Å^2		*x/a*	*y/b*	*z/c*	U,^{a} Å^2
Cation A									
Au	0.61167 (9)	0.13628 (8)	0.27931 (7)	0.046	C(G2)	0.6376 (17)	0.0530 (24)	0.1628 (12)	0.033 (9)
Pt(1)	0.94537 (8)	0.18177 (7)	0.26225 (6)	0.033	C(G3)	0.6102 (17)	−0.0073 (15)	0.1334 (16)	0.058 (12)
Pt(2)	0.87511 (8)	0.18892 (7)	0.17450 (6)	0.033	C(G4)	0.5612 (25)	−0.0001 (18)	0.0912 (11)	0.078 (14)
Pt(3)	0.73610 (8)	0.18777 (7)	0.25710 (6)	0.034	C(G5)	0.5396 (17)	0.0675 (24)	0.0784 (12)	0.089 (15)
Ag	0.82940 (16)	0.07792 (14)	0.22862 (13)	0.051	C(G6)	0.5670 (17)	0.1278 (15)	0.1078 (16)	0.069 (13)
Cl	0.8534 (7)	−0.0494 (5)	0.2267 (5)	0.100	C(H1)	0.5791 (22)	0.2606 (14)	0.2002 (18)	0.035 (10)
S	0.8438 (5)	0.2528 (4)	0.2398 (4)	0.041	C(H2)	0.5020 (27)	0.2473 (19)	0.1843 (11)	0.070 (13)
P(1)	1.0445 (5)	0.1160 (5)	0.2433 (4)	0.036	C(H3)	0.4485 (16)	0.2956 (24)	0.1976 (13)	0.072 (13)
P(2)	0.9576 (5)	0.1166 (5)	0.1418 (4)	0.040	C(H4)	0.4722 (22)	0.3572 (14)	0.2267 (18)	0.093 (16)
P(3)	0.7799 (5)	0.2242 (5)	0.1175 (4)	0.039	C(H5)	0.5493 (27)	0.3705 (19)	0.2426 (11)	0.071 (13)
P(4)	0.6570 (5)	0.2013 (5)	0.1868 (4)	0.040	C(H6)	0.6028 (16)	0.3222 (24)	0.2293 (13)	0.059 (12)
P(5)	0.7757 (5)	0.1789 (5)	0.3374 (4)	0.039	C(I1)	0.7134 (21)	0.2343 (12)	0.3712 (17)	0.050 (11)
P(6)	0.9569 (5)	0.2004 (5)	0.3420 (4)	0.040	C(I2)	0.7027 (12)	0.3042 (9)	0.3594 (8)	0.046 (11)
P(7)	0.5019 (6)	0.0998 (5)	0.3048 (4)	0.051	C(I3)	0.6511 (18)	0.3471 (13)	0.3802 (15)	0.074 (14)
C(1)	1.0134 (19)	0.0638 (18)	0.1859 (15)	0.051 (11)	C(I4)	0.6103 (21)	0.3199 (12)	0.4127 (17)	0.074 (14)
C(2)	0.6947 (18)	0.2571 (16)	0.1447 (14)	0.040 (10)	C(I5)	0.6210 (12)	0.2500 (9)	0.4245 (8)	0.068 (13)
C(3)	0.8651 (18)	0.2280 (16)	0.3626 (14)	0.039 (10)	C(I6)	0.6725 (18)	0.2072 (13)	0.4037 (15)	0.060 (12)
C(A1)	1.0965 (12)	0.0499 (23)	0.2822 (17)	0.055 (12)	C(J1)	0.7856 (14)	0.0951 (14)	0.3637 (15)	0.036 (10)
C(A2)	1.1391 (25)	0.0776 (13)	0.3249 (16)	0.061 (12)	C(J2)	0.8115 (23)	0.0916 (17)	0.4120 (13)	0.047 (11)
C(A3)	1.1818 (25)	0.0324 (26)	0.3543 (8)	0.082 (15)	C(J3)	0.8211 (18)	0.0256 (22)	0.4306 (10)	0.073 (13)
C(A4)	1.1818 (12)	−0.0405 (23)	0.3411 (17)	0.062 (12)	C(J4)	0.8048 (14)	−0.0369 (14)	0.4009 (15)	0.077 (14)
C(A5)	1.1393 (25)	−0.0682 (13)	0.2984 (16)	0.082 (14)	C(J5)	0.7789 (23)	−0.0333 (17)	0.3526 (13)	0.062 (12)
C(A6)	1.0966 (25)	−0.0230 (26)	0.2689 (8)	0.098 (16)	C(J6)	0.7693 (18)	0.0326 (22)	0.3341 (10)	0.059 (12)
C(B1)	1.1234 (16)	0.1773 (17)	0.2364 (8)	0.033 (9)	C(K1)	0.9859 (11)	0.1254 (16)	0.3795 (14)	0.029 (9)
C(B2)	1.1188 (18)	0.2499 (15)	0.2497 (17)	0.043 (10)	C(K2)	0.9745 (19)	0.0558 (21)	0.3588 (8)	0.036 (10)
C(B3)	1.1803 (24)	0.2953 (11)	0.2483 (15)	0.067 (13)	C(K3)	0.9942 (22)	−0.0014 (13)	0.3858 (13)	0.056 (12)
C(B4)	1.2464 (16)	0.2682 (17)	0.2337 (8)	0.071 (13)	C(K4)	1.0254 (11)	0.0110 (16)	0.4335 (14)	0.051 (11)
C(B5)	1.2509 (18)	0.1956 (15)	0.2205 (17)	0.095 (16)	C(K5)	1.0368 (19)	0.0806 (21)	0.4543 (8)	0.083 (15)
C(B6)	1.1894 (24)	0.1502 (11)	0.2218 (15)	0.067 (13)	C(K6)	1.0171 (22)	0.1378 (13)	0.4273 (13)	0.052 (11)
C(C1)	1.0319 (14)	0.1663 (16)	0.1221 (8)	0.034 (9)	C(L1)	1.0227 (24)	0.2781 (19)	0.3610 (9)	0.040 (10)
C(C2)	1.0307 (20)	0.2402 (14)	0.1302 (18)	0.058 (12)	C(L2)	1.0948 (18)	0.2736 (17)	0.3874 (17)	0.058 (12)
C(C3)	1.0896 (24)	0.2818 (11)	0.1194 (16)	0.093 (16)	C(L3)	1.1399 (17)	0.3350 (26)	0.4005 (15)	0.082 (14)
C(C4)	1.1498 (14)	0.2495 (16)	0.1006 (8)	0.087 (15)	C(L4)	1.1128 (24)	0.4007 (19)	0.3872 (9)	0.079 (14)
C(C5)	1.1511 (20)	0.1755 (14)	0.0925 (18)	0.083 (15)	C(L5)	1.0407 (18)	0.4051 (17)	0.3607 (17)	0.092 (16)
C(C6)	1.0921 (24)	0.1339 (11)	0.1032 (16)	0.080 (14)	C(L6)	0.9956 (17)	0.3438 (26)	0.3476 (15)	0.074 (14)
C(D1)	0.9220 (24)	0.0508 (20)	0.0934 (10)	0.039 (10)	C(M11)	0.4376 (25)	0.0435 (23)	0.2605 (9)	0.046 (11)
C(D2)	0.8801 (18)	−0.0065 (17)	0.1044 (8)	0.050 (11)	C(M12)	0.3857 (21)	−0.0042 (19)	0.2732 (8)	0.070 (13)
C(D3)	0.8491 (14)	−0.0580 (11)	0.0687 (9)	0.077 (14)	C(M13)	0.3351 (13)	−0.0430 (12)	0.2381 (8)	0.074 (14)
C(D4)	0.8598 (24)	−0.0522 (20)	0.0220 (10)	0.078 (14)	C(M14)	0.3363 (25)	−0.0340 (23)	0.1904 (9)	0.086 (15)
C(D5)	0.9017 (18)	0.0052 (17)	0.0109 (8)	0.075 (14)	C(M15)	0.3882 (21)	0.0137 (19)	0.1777 (8)	0.088 (15)
C(D6)	0.9327 (14)	0.0567 (11)	0.0466 (9)	0.046 (11)	C(M16)	0.4388 (13)	0.0525 (12)	0.2128 (8)	0.077 (14)
C(E1)	0.8063 (13)	0.3034 (10)	0.0891 (10)	0.046 (11)	C(M21)	0.4436 (25)	0.1746 (14)	0.3241 (20)	0.061 (12)
C(E2)	0.7693 (17)	0.3683 (13)	0.0912 (15)	0.054 (11)	C(M22)	0.4673 (12)	0.2452 (18)	0.3241 (14)	0.066 (13)
C(E3)	0.7939 (21)	0.4251 (14)	0.0688 (18)	0.064 (12)	C(M23)	0.4210 (23)	0.3004 (14)	0.3374 (13)	0.066 (13)
C(E4)	0.8555 (13)	0.4170 (10)	0.0443 (10)	0.082 (15)	C(M24)	0.3511 (25)	0.2848 (14)	0.3507 (20)	0.077 (14)
C(E5)	0.8925 (17)	0.3521 (13)	0.0422 (15)	0.074 (14)	C(M25)	0.3274 (12)	0.2142 (18)	0.3507 (14)	0.108 (18)
C(E6)	0.8680 (21)	0.2953 (14)	0.0646 (18)	0.066 (13)	C(M26)	0.3737 (23)	0.1590 (14)	0.3374 (13)	0.093 (16)
C(F1)	0.7364 (27)	0.1662 (27)	0.0649 (12)	0.066 (13)	C(M31)	0.5265 (12)	0.0510 (21)	0.3582 (14)	0.047 (11)
C(F2)	0.7318 (15)	0.0927 (27)	0.0672 (15)	0.065 (13)	C(M32)	0.5098 (19)	0.0756 (14)	0.4027 (19)	0.063 (12)
C(F3)	0.7000 (22)	0.0488 (12)	0.0273 (19)	0.088 (15)	C(M33)	0.5346 (23)	0.0383 (16)	0.4421 (12)	0.071 (13)
C(F4)	0.6729 (27)	0.0784 (27)	−0.0149 (12)	0.104 (17)	C(M34)	0.5761 (12)	−0.0236 (21)	0.4370 (14)	0.093 (16)
C(F5)	0.6775 (15)	0.1519 (27)	−0.0173 (15)	0.140 (22)	C(M35)	0.5929 (19)	−0.0481 (14)	0.3925 (19)	0.075 (14)
C(F6)	0.7092 (22)	0.1958 (12)	0.0226 (19)	0.090 (15)	C(M36)	0.5680 (23)	−0.0109 (16)	0.3531 (12)	0.053 (11)
C(G1)	0.6160 (25)	0.1206 (18)	0.1500 (11)	0.036 (10)					
Cation B									
Au	0.47691 (9)	0.37094 (8)	0.78804 (7)	0.042	C(A4)	1.0362 (24)	0.5552 (21)	0.8251 (8)	0.068 (13)
Pt(1)	0.80396 (8)	0.30868 (7)	0.75340 (6)	0.034	C(A5)	1.0463 (15)	0.4839 (24)	0.8337 (13)	0.065 (13)
Pt(2)	0.71765 (8)	0.28921 (7)	0.66925 (6)	0.033	C(A6)	1.0025 (18)	0.4309 (12)	0.8047 (15)	0.051 (11)
Pt(3)	0.59501 (8)	0.30886 (7)	0.76117 (6)	0.032	C(B1)	0.9739 (23)	0.3207 (18)	0.7134 (21)	0.047 (11)
Ag	0.68732 (16)	0.41019 (14)	0.73040 (13)	0.050	C(B2)	0.9707 (13)	0.2467 (18)	0.7131 (11)	0.064 (13)
Cl	0.6944 (8)	0.5373 (5)	0.7260 (5)	0.093	C(B3)	1.0300 (25)	0.2061 (12)	0.6993 (17)	0.092 (16)
S	0.6962 (5)	0.2375 (4)	0.7360 (4)	0.037	C(B4)	1.0925 (23)	0.2395 (18)	0.6860 (21)	0.105 (17)
P(1)	0.8971 (5)	0.3734 (5)	0.7298 (4)	0.037	C(B5)	1.0956 (13)	0.3135 (18)	0.6863 (11)	0.117 (19)
P(2)	0.7958 (5)	0.3542 (5)	0.6322 (4)	0.035	C(B6)	1.0363 (25)	0.3541 (12)	0.7001 (17)	0.097 (16)
P(3)	0.6131 (5)	0.2436 (4)	0.6164 (4)	0.034	C(C1)	0.8623 (27)	0.2996 (14)	0.6041 (20)	0.050 (11)
P(4)	0.5070 (5)	0.2763 (4)	0.6953 (4)	0.036	C(C2)	0.9169 (26)	0.3285 (13)	0.5808 (17)	0.087 (15)
P(5)	0.6446 (5)	0.3340 (5)	0.8391 (4)	0.038	C(C3)	0.9641 (12)	0.2837 (15)	0.5576 (11)	0.120 (19)
P(6)	0.8248 (5)	0.3085 (5)	0.8356 (4)	0.039	C(C4)	0.9568 (27)	0.2100 (14)	0.5579 (20)	0.138 (22)
P(7)	0.3707 (6)	0.4150 (5)	0.8152 (4)	0.051	C(C5)	0.9022 (26)	0.1811 (13)	0.5812 (17)	0.121 (20)
C(1)	0.8593 (19)	0.4129 (17)	0.6756 (15)	0.047 (11)	C(C6)	0.8550 (12)	0.2259 (15)	0.6043 (11)	0.065 (13)
C(2)	0.5363 (17)	0.2155 (15)	0.6482 (13)	0.029 (9)	C(D1)	0.7520 (10)	0.4148 (20)	0.5879 (16)	0.041 (10)
C(3)	0.7362 (17)	0.2898 (15)	0.8593 (13)	0.028 (9)	C(D2)	0.7524 (22)	0.3990 (10)	0.5395 (18)	0.059 (12)
C(A1)	0.9487 (24)	0.4493 (21)	0.7671 (8)	0.045 (11)	C(D3)	0.7228 (22)	0.4471 (19)	0.5074 (10)	0.075 (14)
C(A2)	0.9387 (15)	0.5206 (24)	0.7585 (13)	0.056 (12)	C(D4)	0.6927 (10)	0.5110 (20)	0.5236 (16)	0.080 (14)
C(A3)	0.9825 (18)	0.5736 (12)	0.7875 (15)	0.067 (13)	C(D5)	0.6923 (22)	0.5268 (10)	0.5720 (18)	0.073 (13)

Table III (Continued)

	x/*a*	*y*/*b*	*z*/*c*	U,[a] Å^2		*x*/*a*	*y*/*b*	*z*/*c*	U,[a] Å^2
C(D6)	0.7219 (22)	0.4787 (19)	0.6042 (10)	0.073 (14)	C(J4)	0.6795 (23)	0.5592 (14)	0.9171 (13)	0.068 (13)
C(E1)	0.6393 (23)	0.1617 (10)	0.5919 (16)	0.040 (10)	C(J5)	0.7080 (20)	0.5005 (22)	0.9401 (9)	0.070 (13)
C(E2)	0.6263 (15)	0.0934 (10)	0.5946 (10)	0.057 (12)	C(J6)	0.6978 (12)	0.4323 (17)	0.9168 (15)	0.033 (9)
C(E3)	0.6558 (16)	0.0346 (10)	0.5712 (12)	0.054 (11)	C(K1)	0.8621 (24)	0.3945 (15)	0.8674 (11)	0.033 (9)
C(E4)	0.6982 (23)	0.0441 (10)	0.5351 (16)	0.055 (12)	C(K2)	0.9135 (14)	0.3983 (16)	0.9095 (15)	0.045 (11)
C(E5)	0.7112 (15)	0.1124 (10)	0.5223 (10)	0.085 (15)	C(K3)	0.9356 (18)	0.4644 (23)	0.9336 (10)	0.066 (13)
C(E6)	0.6817 (16)	0.1712 (10)	0.5458 (12)	0.065 (13)	C(K4)	0.9062 (24)	0.5266 (15)	0.9154 (11)	0.062 (12)
C(F1)	0.5592 (12)	0.2894 (23)	0.5694 (14)	0.039 (10)	C(K5)	0.8548 (14)	0.5228 (16)	0.8733 (15)	0.066 (13)
C(F2)	0.5665 (24)	0.3631 (24)	0.5694 (7)	0.038 (10)	C(K6)	0.8327 (18)	0.4567 (23)	0.8492 (10)	0.043 (10)
C(F3)	0.5245 (21)	0.3983 (10)	0.5334 (14)	0.074 (14)	C(L1)	0.8811 (15)	0.2349 (20)	0.8610 (20)	0.041 (10)
C(F4)	0.4753 (12)	0.3598 (23)	0.4974 (14)	0.101 (17)	C(L2)	0.8698 (23)	0.2106 (11)	0.9041 (19)	0.086 (15)
C(F5)	0.4680 (24)	0.2861 (24)	0.4974 (7)	0.103 (17)	C(L3)	0.9123 (18)	0.1543 (18)	0.9221 (9)	0.109 (18)
C(F6)	0.5099 (21)	0.2509 (10)	0.5334 (14)	0.046 (11)	C(L4)	0.9661 (15)	0.1224 (20)	0.8970 (20)	0.082 (15)
C(G1)	0.4600 (12)	0.3444 (19)	0.6605 (15)	0.031 (9)	C(L5)	0.9773 (23)	0.1467 (11)	0.8539 (19)	0.091 (16)
C(G2)	0.4859 (20)	0.4147 (24)	0.6713 (10)	0.070 (13)	C(L6)	0.9348 (18)	0.2029 (18)	0.8359 (9)	0.084 (15)
C(G3)	0.4535 (23)	0.4681 (14)	0.6444 (11)	0.058 (12)	C(M11)	0.3083 (13)	0.4699 (22)	0.7768 (18)	0.045 (11)
C(G4)	0.3950 (12)	0.4513 (19)	0.6066 (15)	0.085 (15)	C(M12)	0.2562 (24)	0.5154 (20)	0.7948 (10)	0.070 (13)
C(G5)	0.3691 (20)	0.3809 (24)	0.5958 (10)	0.068 (13)	C(M13)	0.2060 (21)	0.5530 (11)	0.7642 (20)	0.066 (13)
C(G6)	0.4016 (23)	0.3275 (14)	0.6227 (11)	0.053 (11)	C(M14)	0.2078 (13)	0.5451 (22)	0.7154 (18)	0.081 (14)
C(H1)	0.4321 (12)	0.2210 (11)	0.7148 (7)	0.043 (10)	C(M15)	0.2598 (24)	0.4996 (20)	0.6974 (10)	0.104 (17)
C(H2)	0.3551 (14)	0.2366 (17)	0.7111 (15)	0.064 (13)	C(M16)	0.3101 (21)	0.4620 (11)	0.7281 (20)	0.070 (13)
C(H3)	0.3065 (12)	0.1938 (20)	0.7309 (16)	0.074 (14)	C(M21)	0.3063 (17)	0.3412 (14)	0.8260 (7)	0.051 (11)
C(H4)	0.3348 (12)	0.1354 (11)	0.7544 (7)	0.066 (13)	C(M22)	0.2283 (14)	0.3416 (19)	0.8102 (16)	0.061 (12)
C(H5)	0.4118 (14)	0.1198 (17)	0.7580 (15)	0.068 (13)	C(M23)	0.1820 (15)	0.2860 (24)	0.8192 (15)	0.079 (14)
C(H6)	0.4604 (12)	0.1626 (20)	0.7382 (16)	0.056 (12)	C(M24)	0.2138 (17)	0.2301 (14)	0.8439 (7)	0.073 (13)
C(I1)	0.5858 (10)	0.2843 (11)	0.8759 (7)	0.063 (12)	C(M25)	0.2918 (14)	0.2297 (19)	0.8597 (16)	0.069 (13)
C(I2)	0.5555 (24)	0.3140 (15)	0.9151 (13)	0.060 (12)	C(M26)	0.3380 (15)	0.2853 (24)	0.8507 (15)	0.078 (14)
C(I3)	0.5092 (23)	0.2726 (13)	0.9376 (14)	0.086 (15)	C(M31)	0.3912 (26)	0.4717 (23)	0.8710 (11)	0.037 (10)
C(I4)	0.4933 (10)	0.2016 (11)	0.9210 (7)	0.064 (12)	C(M32)	0.3781 (18)	0.4503 (14)	0.9145 (12)	0.062 (12)
C(I5)	0.5236 (24)	0.1719 (15)	0.8819 (13)	0.063 (12)	C(M33)	0.4020 (16)	0.4938 (18)	0.9561 (9)	0.088 (15)
C(I6)	0.5698 (23)	0.2133 (13)	0.8594 (14)	0.062 (12)	C(M34)	0.4389 (26)	0.5587 (23)	0.9541 (11)	0.094 (16)
C(J1)	0.6592 (23)	0.4229 (14)	0.8704 (13)	0.039 (10)	C(M35)	0.4520 (18)	0.5800 (14)	0.9105 (12)	0.092 (16)
C(J2)	0.6306 (20)	0.4816 (22)	0.8474 (9)	0.056 (12)	C(M36)	0.4281 (16)	0.5365 (18)	0.8690 (9)	0.080 (14)
C(J3)	0.6408 (12)	0.5498 (17)	0.8707 (15)	0.064 (13)					
					$[PF_6]^-$ Anions				
P(F1)	0.3570 (6)	0.2072 (6)	0.0294 (5)	0.109	P(F2)	0.2530 (8)	0.1933 (6)	0.5031 (6)	0.161
F(11)	0.4403 (15)	0.2276 (24)	0.0503 (12)	0.220 (18)	F(21)	0.2782 (16)	0.2703 (8)	0.4974 (11)	0.176 (14)
F(12)	0.2737 (15)	0.1868 (24)	0.0085 (12)	0.288 (25)	F(22)	0.2277 (16)	0.1163 (8)	0.5087 (11)	0.160 (13)
F(13)	0.3586 (8)	0.2607 (15)	−0.0085 (11)	0.198 (17)	F(23)	0.1729 (13)	0.2198 (14)	0.5094 (18)	0.178 (15)
F(14)	0.3555 (8)	0.1538 (15)	0.0674 (11)	0.243 (21)	F(24)	0.3330 (13)	0.1668 (14)	0.4967 (18)	0.239 (21)
F(15)	0.3293 (26)	0.2664 (10)	0.0631 (16)	0.199 (16)	F(25)	0.2788 (23)	0.2055 (20)	0.5573 (7)	0.296 (28)
F(16)	0.3848 (26)	0.1480 (10)	−0.0042 (16)	0.327 (30)	F(26)	0.2271 (23)	0.1811 (20)	0.4489 (7)	0.195 (17)

[a] For C and F atoms *U* is the refined isotropic displacement parameter; for Au, Pt, Ag, S, and P atoms it is the mean of the principal values of the anisotropic displacement tensor (see Table SIII).

trans influence on Pt–S bonds; a similar perturbation of the Pt–S distances in **1** was ascribed[13] to the high trans influence of H$^-$; in **3**, however, where the CN$^-$ ion exerts a lower trans influence, all three Pd–S distances are equal.

A notable feature of **2** is the presence of a short Pt–Au bond [mean length 2.576 (2) Å] that is not supported by bridging groups. In triangular[3,12] and linear[6] heterometallic PtAu clusters the Pt–Au distances are typically 2.60–2.67 Å, with the value of 2.600 (3) Å in $[PtCl(AuPPh_3)_2(PEt_3)_2]^+$ being closest to that found here. In Au_2Pt_2 butterfly[10] and Pt_3Au tetrahedral[16] clusters the Pt–Au bonds are longer than 2.71 Å. In **2** the Au atoms have nearly linear coordination (mean Pt–Au–P angle 174°). They do not appear to be involved in close contacts with the surrounding phenyl rings: the shortest intramolecular Au···H(phenyl) distance is 2.92 Å (to ring J in cation B), and all other Au···H contacts are longer than 3 Å.

A structural feature unique to **2** is the presence of the capping AgCl unit. In both A and B the Ag atom is slightly closer to Pt(3) [Pt(3)–Ag = 2.780 (4) and 2.768 (4) Å] than it is to Pt(1) or Pt(2) [Pt–Ag = 2.808 (4)–2.861 (4)Å]. In B the Ag atom is equidistant from Pt(1) and Pt(2) whereas in A these distances differ by 0.05 Å. These Pt–Ag distances are comparable with the values found in complexes where Ag bridges two or more Pt atoms (2.74–3.06 Å),[8,9,17] but they are appreciably longer than the unsupported Pt–Ag bond length of 2.637 (1) Å in $[(C_4H_8S)(C_6F_5)_3PtAgPPh_3]$.[19] The terminal Ag–Cl distances [2.39 (1) and 2.41 (1) Å] are comparable to the shortest Ag–Cl distances in $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$, where the Cl ligands bridge Pt–Ag bonds.[17] Corresponding Pt–Ag–Cl angles in A and B differ by up to 9° (see Table I).

The six-membered Pt(3)SPtPCP rings containing the atoms C(2) and C(3) display skew-boat conformations with S–Pt(3)–P–C torsion angles close to zero. The corresponding rings in **1** and **3** adopt similar conformations.[13,14] Also in common with **1** and **3**, the $Pt_2P_2C(1)$ rings display envelope conformations characterized by P(1)–Pt(1)–Pt(2)–P(2) torsion angles of less than 5°. However, in **2** the C(1) flap is folded towards the AgCl side of the Pt_3 plane, rather than towards the S side (as in **1** and **3**). This conformational change helps to accommodate the AgCl unit, which fits snugly into a hydrophobic cavity defined by the C(1) methylene group and the phenyl rings A, D, F, G, J, and K. The shortest Ag···H and Cl···H contacts with the sides of the cavity

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(16) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* **1984**, *267*, C52. Briant, C. E.; Wardle, R. W. M.; Mingos, D. M. P. *J. Organomet. Chem.* **1984**, *267*, C49. Mingos, D. M. P.; Wardle, R. W. M. *J. Chem. Soc., Dalton Trans.* **1986**, 73.

(17) Usón, R.; Fornies, J.; Thomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556. Usón, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Thomas, M. *Inorg. Chem.* **1985**, *24*, 4651.

(18) Cotton, F. A.; Falvello, L. R.; Usón, R.; Fornies, J.; Thomas, M.; Casas, J. M.; Ara, I. *Inorg. Chem.* **1987**, *26*, 1366.

(19) Bos, W.; Bour, J. J.; Schlebos, P. P. J.; Hageman, P.; Bosman, W. P.; Smits, J. M. M.; van Wietermarschen, J. A. C.; Beurskens, P. T. *Inorg. Chim. Acta* **1986**, *119*, 141.

are respectively 2.79 and 2.77 Å for cation A and 2.87 and 2.69 Å for cation B.

The NMR data for **2** are consistent with the structure determined crystallographically. Thus, the ^{31}P NMR data are similar to those of **1** and are characteristic of a $Pt_3(dppm)_3$ complex with only one Pt–Pt bond.[13] The ^{1}H NMR spectrum contained resonances due to nonequivalent $P_2CH^aH^b$ protons of the dppm ligands, indicating that there is no plane of symmetry containing the $Pt_3(dppm)_3$ unit. In complex **1**, similar features are observed in the low-temperature ^{1}H NMR spectrum, but a fluxional process, involving inversion of the $Pt_3(\mu_3\text{-}S)$ unit, leads to the effective equivalence of the $P_2CH^aH^b$ protons at room temperature.[13] In complex **2**, this inversion is clearly prevented from occurring by the presence of the μ_3-AgCl ligand.

If we consider formation of **2** to occur by addition of the electron-poor AgCl fragment to the electron-rich $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu\text{-dppm})_3]^+$ unit (having a structure similar to that of **1**), it is interesting that AgCl adds to the electron-rich platinum atoms rather than to the sulfido ligand, which still carries a lone pair of electrons and should have donor properties.[19] We have attempted to synthesize higher clusters by addition of 2 or more equiv of $[Au(NO_3)(PPh_3)]$ or $[Au(NO_3)(PPh_3)]$/AgCl to complex **1**, but we have been unable to isolate pure compounds from such reactions. It is therefore not clear if further cluster building via the sulfido ligand is possible. The isolation of **2** was unexpected, but the cluster is interesting as the first PtAuAg cluster. While there is no Au–Ag bonding, the unbridged Pt–Au bond and the $Pt_3(\mu_3\text{-}AgCl)$ unit with only one Pt–Pt bond are both, so far as we know, unprecedented.

Experimental Section

NMR spectra were recorded by using a Varian XL200 or XL300 spectrometer, with an internal Me_4Si (^{1}H) or an external H_3PO_4 (^{31}P) reference. The complex $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]PF_6$ (**1**) was prepared by the literature method.[13]

$[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$. To a solution of **1** (84.1 mg, 0.0465 mmol) in CH_2Cl_2 (10 mL) was added a mixture prepared by reaction of $[AuCl(PPh_3)]$ (23.2 mg, 0.0469 mmol) in CH_2Cl_2 (5 mL) with $AgNO_3$ (9.7 mg, 0.0571 mmol) in CH_3OH (5 mL). After this mixture was stirred for 5 min, water (20 mL) was added, the layers were separated, and the organic layer was dried over $MgSO_4$. The volume was reduced under vacuum, and NH_4PF_6 in methanol was added to precipitate the product, which was recrystallized from acetone/pentane. Yield: 53%. Mp: 175 °C dec. Anal. Calcd for $C_{93}H_{81}AgAuClF_6P_8Pt_3S$: C, 44.4; H, 3.2. Found: C, 44.6; H, 3.3%. NMR in acetone-d_6: ^{1}H, δ 6.04 [m, 2 H, $^2J(H^aH^b)$ = 12 Hz, $C^2H^aH^b$], 4.2 [d, 2 H, $^2J(H^aH^b)$ = 12 Hz, $C^1H^aH^b$], 3.6 [d, 2 H, $C^1H^aH^b$]; ^{31}P, δ 35.0 [s, $^2J(PtP)$ = 667 Hz, *P*Au], 31.2 [s, $^1J(PtP^a)$ = 3120 Hz, P^a], 5.9 [t, $^2J(PP)$ = 20 Hz, $^3J(P^bP^{b'})$ = 156 Hz, $^1J(PtP^b)$ = 3168 Hz, $^2J(PtP^b)$ = 132 Hz, P^b], −17.2 [t, $^2J(PP)$ = 20 Hz, $^1J(PtP^c)$ = 3576 Hz, P^c].

X-ray Analysis of $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$ (2). The specimen was a transparent red crystal, grown from acetone/pentane and mounted in air. All crystallographic measurements were made on an Enraf-Nonius CAD4F diffractometer using Mo X-rays and a graphite monochromator. The dimensions of the reduced triclinic cell (Table II) are based on a least-squares fit to the setting angles of 22 reflections with $11 \leq \theta \leq 14°$. The measured intensities were corrected for *Lp* effects, and an empirical absorption correction was applied.[20] During data collection the intensities of two standard reflections showed only random fluctuations of ±5% about their mean values.

The structure was solved successfully in the space group $P\bar{1}$. The metal atoms were located by direct methods,[21] and the remaining non-hydrogen atoms were found from subsequent difference syntheses. In the final calculations fixed contributions were added to the structure factors to account for the scattering of all 162 hydrogen atoms: they were assigned a common isotropic displacement parameter U = 0.10 Å, and their positions were deduced geometrically, assuming C–H = 0.96 Å. For Au, Pt, Ag, Cl, S, and P atoms anisotropic displacement parameters were refined, whereas isotropic displacement parameters were adjusted for F and C atoms. The 30 phenyl rings were refined as planar rigid groups with C–C = 1.38 Å and ∠C–C–C = 120°. The PF_6 anions were also refined as rigid groups with P–F = 1.53 Å and ∠F–P–F = 90 or 180°. In alternate full-matrix least-squares calculations, the parameters of cation A, together with those of the PF_6^- anions, and then those of cation B were refined. Atomic parameters for **2** are given in Table III. The most prominent features of the final difference synthesis (ca. 2 e Å^{-3} are associated with a site partially occupied by a disordered solvent molecule. We were unable to model this feature successfully. Mean $w\Delta^2$ showed no consistent variation with $|F|$ but increased at low $(\sin\theta)/\lambda$.

Neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 22. Calculations were performed on a Gould 3227 32-bit minicomputer using the locally developed GX program package.[23]

Acknowledgment. We thank the NSERC (Canada) for financial support (to R.J.P.), the SERC (Great Britain) for a studentship (to G.D.), and NATO for a travel grant.

Supplementary Material Available: Tables SI–SIV, listing experimental details of the structure determination, derived hydrogen positions, anisotropic displacement parameters, and interbond angles (12 pages); Table SV, listing calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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(20) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(21) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(22) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99 and 149.

(23) Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.

Additions and Corrections

1987, Volume 26

Teddy G. Traylor* and Shinji Tsuchiya: Perhalogenated Tetraphenylhemins: Stable Catalysts of High Turnover Catalytic Hydroxylations.

Page 1338. In Table I, the porphyrin has a shoulder at 643 and not 603 nm, and the zinc complex has a shoulder at 660 and not 600 nm. In addition, the bromination must be carried out under scrupulous anhydrous conditions.—Teddy G. Traylor

1988, Volume 27

Johann W. Buchler,* André de Cian, Jean Fischer, Martina Kihn-Botulinski, and Raymond Weiss*: Metal Complexes with Tetrapyrrole Ligands. 46. Europium(III) Bis(octaethylporphyrinate), a Lanthanoid Porphyrin Sandwich with Porphyrin Rings in Different Oxidation States, and Dieuropium(III) Tris(octaethylporphyrinate).

Page 340. Reference 10 should have appeared as follows: (a) Lux, F.; ... (as given). (b) Girolami, G. S.; Milam, S. N.; Suslick, K. N. *Inorg. Chem.* **1987**, *26*, 343–344. References 10a and 10b are correctly cited in the corresponding text.

Page 341. In the left column, second complete paragraph, the fourth complete sentence should read as follows: It did not show any absorption in the near-infrared region (900–2000 nm).—Johann W. Buchler