

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  $^{31}\text{P}$  NMR data are similar to those of **1** and are characteristic of a  $\text{Pt}_3(\text{dppm})_3$  complex with only one Pt–Pt bond.<sup>13</sup> The  $^1\text{H}$  NMR spectrum contained resonances due to nonequivalent  $\text{P}_2\text{CH}^a\text{H}^b$  protons of the dppm ligands, indicating that there is no plane of symmetry containing the  $\text{Pt}_3(\text{dppm})_3$  unit. In complex **1**, similar features are observed in the low-temperature  $^1\text{H}$  NMR spectrum, but a fluxional process, involving inversion of the  $\text{Pt}_3(\mu_3\text{-S})$  unit, leads to the effective equivalence of the  $\text{P}_2\text{CH}^a\text{H}^b$  protons at room temperature.<sup>13</sup> In complex **2**, this inversion is clearly prevented from occurring by the presence of the  $\mu_3\text{-AgCl}$  ligand.

If we consider formation of **2** to occur by addition of the electron-poor AgCl fragment to the electron-rich  $[\text{Pt}_3(\mu_3\text{-S})(\text{AuPPh}_3)(\mu\text{-dppm})_3]^+$  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.<sup>19</sup> We have attempted to synthesize higher clusters by addition of 2 or more equiv of  $[\text{Au}(\text{NO}_3)(\text{PPh}_3)]$  or  $[\text{Au}(\text{NO}_3)(\text{PPh}_3)]/\text{AgCl}$  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  $\text{Pt}_3(\mu_3\text{-AgCl})$  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  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ) or an external  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) reference. The complex  $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3]\text{PF}_6$  (**1**) was prepared by the literature method.<sup>13</sup>

$[\text{Pt}_3(\mu_3\text{-S})(\text{AuPPh}_3)(\mu_3\text{-AgCl})(\mu\text{-dppm})_3]\text{PF}_6$ . To a solution of **1** (84.1 mg, 0.0465 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added a mixture prepared by reaction of  $[\text{AuCl}(\text{PPh}_3)]$  (23.2 mg, 0.0469 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) with  $\text{AgNO}_3$  (9.7 mg, 0.0571 mmol) in  $\text{CH}_3\text{OH}$  (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  $\text{MgSO}_4$ . The volume was reduced under vacuum, and  $\text{NH}_4\text{PF}_6$  in methanol was added to precipitate the product, which was recrystallized from acetone/pentane. Yield: 53%. Mp: 175 °C dec. Anal. Calcd for  $\text{C}_{93}\text{H}_{81}\text{AgAuClF}_6\text{P}_8\text{Pt}_3\text{S}$ : C, 44.4; H, 3.2. Found: C, 44.6; H, 3.3%. NMR in acetone- $d_6$ :  $^1\text{H}$ ,  $\delta$  6.04 [m, 2 H,  $^2J(\text{H}^a\text{H}^b) = 12$  Hz,  $\text{C}^2\text{H}^a\text{H}^b$ ], 4.2 [d, 2 H,  $^2J(\text{H}^a\text{H}^b) = 12$  Hz,  $\text{C}^1\text{H}^a\text{H}^b$ ], 3.6 [d, 2 H,  $\text{C}^1\text{H}^a\text{H}^b$ ];  $^{31}\text{P}$ ,  $\delta$  35.0 [s,  $^2J(\text{PtP}) = 667$  Hz,  $\text{PAu}$ ], 31.2 [s,  $^1J(\text{PtP}^a) = 3120$  Hz,  $\text{P}^a$ ], 5.9 [t,  $^2J(\text{PP}) = 20$  Hz,  $^3J(\text{P}^b\text{P}^b) =$

156 Hz,  $^1J(\text{PtP}^b) = 3168$  Hz,  $^2J(\text{PtP}^b) = 132$  Hz,  $\text{P}^b$ ],  $-17.2$  [t,  $^2J(\text{PP}) = 20$  Hz,  $^1J(\text{PtP}^c) = 3576$  Hz,  $\text{P}^c$ ].

**X-ray Analysis of  $[\text{Pt}_3(\mu_3\text{-S})(\text{AuPPh}_3)(\mu_3\text{-AgCl})(\mu\text{-dppm})_3]\text{PF}_6$  (**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  $11 \leq \theta \leq 14^\circ$ . The measured intensities were corrected for  $Lp$  effects, and an empirical absorption correction was applied.<sup>20</sup> During data collection the intensities of two standard reflections showed only random fluctuations of  $\pm 5\%$  about their mean values.

The structure was solved successfully in the space group  $P\bar{1}$ . The metal atoms were located by direct methods,<sup>21</sup> 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  $\angle\text{C–C–C} = 120^\circ$ . The  $\text{PF}_6$  anions were also refined as rigid groups with P–F = 1.53 Å and  $\angle\text{F–P–F} = 90$  or  $180^\circ$ . In alternate full-matrix least-squares calculations, the parameters of cation A, together with those of the  $\text{PF}_6^-$  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.  $2 e \text{ \AA}^{-3}$ ) 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.<sup>23</sup>

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**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.

(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