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Synthesis and Characterization of Platinum—Gold Clusters Fused to Tetrahedral Copper Units. Crystal Structures of [Pt(PPh₃)(AuPPh₃)₆(Cu₄Cl₃PPh₃)](NO₃) and [Pt(PPh₃)(AuPPh₃)₆(CuI₃)](NO₃)


Contribution from the Department of Inorganic Chemistry and Crystallography, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Abstract: Three new 11-metal-atom Pt—Au—Cu cluster compounds are reported: [Pt(PPh₃)(AuPPh₃)₆(Cu₄Cl₃PPh₃)](NO₃) (1), [Pt(PPh₃)(AuPPh₃)₆(Cu₄Br₃PPh₃)](NO₃) (2) (γ = 0 or 1), and [Pt(PPh₃)(AuPPh₃)(CuI₃)](NO₃) (3). These clusters are obtained from the reaction of [Pt(AuPPh₃)₆(NO₃)₂] with [PtCl₃(PPh₃)₆] (in which X = Cl, Br, or I, respectively). Cluster 1 was characterized by elemental analysis, ICP analysis, FAB-MS, (variable-temperature) ³¹P NMR and ³¹P COSY spectroscopy, ¹⁹⁵Pt NMR spectroscopy, and IR spectroscopy. The crystal and molecular structure of 1 has been determined by a single-crystal X-ray analysis. The compound crystallizes as the NO₃⁻ salt in the monoclinic space group P₂₁/c, with Z = 4, a = 17.871(4) Å, b = 34.687(3) Å, c = 23.357(2) Å, α = 95.49(2)°, β = 94.61(1)°, γ = 109.69(2)°, and V = 8172 Å³. Mo Kα radiation was used. The residuals are R = 0.068 and wR₂ = 0.162 for 11040 observed reflections and 788 variables. Cluster 3 was characterized by ¹⁹⁵Pt NMR spectroscopy and FAB-MS; its solid-state structure was determined by means of a single-crystal X-ray analysis. This cluster compound crystallizes as the NO₃⁻ salt in the triclinic space group P1 with Z = 2, a = 17.501(3) Å, b = 21.152(6) Å, c = 23.581(5) Å, α = 92.18(2)°, β = 94.61(1)°, γ = 109.69(2)°, and V = 8172 Å³. Mo Kα radiation was used. The residuals are R = 0.117 and wR₂ = 0.285 for 2957 observed reflections and 340 variables. Both clusters, 1 and 3, have a tetrahedral Cu₄ unit which is face bonded to the (central) platinum atom, which is furthermore surrounded by six gold {if} moiety, originating from the well-known [PPh₃CuX]₄⁻.

Further additions of M(I) species to the toroidal clusters [Pt(CuCl)(AuPPh₃)₆] and [Pt(Ag)(AuPPh₃)₆] are blocked due to steric arguments, as the metal cluster is restricted to a toroidal geometry because of the presence of only 16 cluster valence electrons. After addition of 2 more electrons (to result in a total number of 18 cluster valence electrons) by nucleophilic addition of a base like PPh₃ or CO, the spherical geometry of the metal cluster allows further growth. So PtCu₄Au₈, PtAg₄Cu₄, and PT₄₈Au₄ frames can only be obtained in spheroidal clusters. It is noteworthy that the solid-state structures of these clusters are such that there are no direct Ag—Ag or Cu—Cu contacts: they are separately distributed among the peripheral metal atoms.

In contrast with these well-known one-by-one atom growth steps, very little is known about the growth of a metal frame by adherence of another multiammonium metal cluster. In this paper we will show that cluster growth occurs by incorporation of a Cu₄ moiety, originating from the well-known [PPh₃CuX]₄⁻. This Cu₄ moiety will be shown to be a Cu₄ moiety, originating from the well-known [PPh₃CuX]₄⁻.

compounds (in which X = Cl, Br, or I). In the newly formed compounds [Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1), [Pt(PPh3)(AuPPh3)(CuCl2Br2PPh3)](NO3) (2) (y = 0 or 1), and [Pt(PPh3)(AuPPh3)(CuCl2)(NO3)] (3) the 4 Cu atoms still hold their original tetrahedral adherence, but now integrated into a PtAuCu cluster frame. So two separate metal clusters merge into a new bigger entity.

Experimental Section

Measurements. Elemental C, H, and N analyses were carried out at the microanalytical department of the University of Nijmegen. ICP analyses giving Pt:Cu ratios were carried out on a Plasma 200 ICP-AES spectrometer in DSMO solutions of the cluster compounds with analyses giving Pt:Au:Cu ratios were carried out on a Plasma 200 ICP-AES spectrometer in DMSO solutions of the cluster compound with the mass spectrometry service laboratory of the University of Minnesota on a VG Analytical Ltd. 7070E-HF mass spectrometer. The FAB-MS spectra were taken in a m-nitrobenzyl alcohol matrix and Csl was used as the mass-standard calibration; further experimental details are published elsewhere.

31P[NH] NMR spectra of CH2Cl2 solutions were recorded on a Bruker WM-200 spectrometer operating at 81.015 MHz and on a Bruker AM-500 spectrometer operating at 202.462 MHz with trimethyl phosphate (TMP) in CDCl3 as external reference. The variable-temperature 31P[NH] NMR spectra were recorded on the Bruker AM-500 spectrometer; the samples used in these experiments contained 100 mg of cluster compound in 1.5 mL of CDCl3.

Proton-decoupled 1H COSY magnitude spectra of CD2Cl2 solutions were recorded on the aforementioned Bruker AM-500 spectrometer at 298 K. The spectra were recorded with equal horizontal resolution in both directions: [Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1) was recorded with 2.0 Hz per point; [Pt(PPh3)(AuPPh3)(CuCl2)](NO3) (3) was recorded with 3.7 Hz per point.

195Pt NMR spectra were recorded at 43.02 MHz on a Bruker WM-200 spectrometer using CD2Cl2 solutions of the compounds; K2PtCl6 in D2O was used as external reference. The infrared (IR) spectra were measured in CsI pellets on a Perkin-Elmer 1720-X Fourier transform infrared spectrometer in the range from 4000 to 220 cm⁻¹.

Preparations. [PPh3CuCl3], [PPh3CuBr3], and [PPh3CuI3] were prepared according to literature methods.8 This is also the case for [Pt(AuPPh3)(NO3)2]. All solvents were of reagent grade and were used without further purification.

[Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1). A 100 mg (0.025 mmol) sample of [Pt(AuPPh3)(NO3)2] was dissolved in 10 mL of acetone, and 31 mg (0.019 mmol) of [PPh3CuCl3] was added. This brown mixture was stirred for 1 h after which it was allowed to stand. After 1 day the reaction mixture had turned red. The solution was then evaporated to dryness and a 1H NMR spectrum of this sample showed that 2 had been formed (yield: about 50%, based on the relative intensities in the 31P NMR spectrum of this crude mixture). Several attempts to purify this mixture were not successful.

Compound 2 has not been analyzed by elemental analysis because the product could not be obtained as pure material. However, comparison of the 31P NMR data of compounds 1, 2, and 3 (see Results and Discussion) together with a comparison of the synthesis procedures of these three compounds, indicates 2 to be closely related to compounds 1 and 3. Therefore, 2 is most probably formulated as [Pt(PPh3)(AuPPh3)(CuBr2PPh3)](NO3) (y = 0 or 1). A 100 mg (0.025 mmol) of [Pt(AuPPh3)(NO3)2] was dissolved in 10 mL of acetone, and 31 mg (0.019 mmol) of [PPh3CuCl3] was added. This brown mixture was stirred for 1 h after which it was allowed to stand. After 1 day the reaction mixture had turned red. The solution was then evaporated to dryness and a 1H NMR spectrum of this sample showed that 2 had been formed (yield: about 50%, based on the relative intensities in the 31P NMR spectrum of this crude mixture). Several attempts to purify this mixture were not successful.

[Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (3). To a solution of 100 mg (0.025 mmol) of [Pt(AuPPh3)(NO3)2] in 10 mL of acetone was added 45.4 mg (0.025 mmol) of [PPh3CuI3] and CuCl. The color changed from brown to orange-red within 5 min and the mixture was stirred for 48 h. The solution was then filtered to remove possible minor solid contaminations. The orange-red filtrate was evaporated to dryness under reduced pressure to yield an orange-red solid in quantitative amounts. Orange-red crystals, all of the same morphology, were obtained by slow diffusion of a dichloromethane solution of this orange-red solid into petroleum ether 40/60. One of these crystals was used for a single-crystal X-ray analysis, which revealed the molecular structure of 3. However, solutions of bulk materials of these crystals (see below) showed the presence of a mixed product in constant ratio to 3. Various attempts to separate these two products were not successful: the 31P NMR spectrum always showed the unchanged ratio of 3 to unknown product as approximately 1:5 (see Results and Discussion).

Compound 3 has not been analyzed by elemental analysis because the product could not be obtained as pure material. Its solid-state structure has been determined by means of a single-crystal X-ray analysis (see below). FAB-MS also confirmed the presence of 3 in the red crystals (see Results and Discussion). 31P NMR: singlet at δ 36.2 ppm (relative intensity 1) with 1J(P-P)(doublet) = 2458 Hz; doublet at δ 50.7 ppm (relative intensity 3) with 1J(P-P)(doublet) = 66 Hz and 2J(P-P)(doublet) = 368 Hz; doublet at δ 57.0 ppm (relative intensity 3) with 1J(P-P)(doublet) = 66 Hz and 2J(P-P)(doublet) = 445 Hz. Shoulders on the doublet peaks indicate that these doublets are a result of closely spaced overlapping signals as seen for compound 1.

The unknown product which was always seen in the 31P NMR spectra together with 3 has the following data: singlet at δ 38.4 ppm with 1J(P-P)(doublet) = 2812 Hz; doublet at δ 45.4 ppm with 1J(P-P)(doublet) = 65 Hz and 2J(P-P)(doublet) = 314 Hz; singlet at δ 2476 Hz; three closely spaced doublets at δ 52.26, 52.31, and 52.27 ppm all with 1J(P-P)(doublet) = 66 Hz and 2J(P-P)(doublet) = 358 Hz; three closely spaced doublets at δ 58.74, 58.80, and 58.88 ppm all with 1J(P-P)(doublet) = 66 Hz and 2J(P-P)(doublet) = 450 Hz. In cases where the horizontal resolution was not high enough, the closely spaced doublets could not be detected separately and two broader doublets were observed at δ 52.3 and 58.8 ppm with corresponding couplings as afore-mentioned; the intensities of both doublets were three times that of the singlet at δ 37.59 ppm. The variable-temperature 31P NMR spectra without proton decoupling was exactly the same, indicating the absence of a dichloromethane solution of this orange-red solid into petroleum ether 40/60. Crystals, all of the same morphology, were obtained by slow diffusion of a dichloromethane solution of this orange-red solid into petroleum ether 40/60. One of these crystals was used for a single-crystal X-ray analysis, which revealed the molecular structure of 3. However, solutions of bulk materials of these crystals (see below) showed the presence of a mixed product in constant ratio to 3. Various attempts to separate these two products were not successful: the 31P NMR spectrum always showed the unchanged ratio of 3 to unknown product as approximately 1:5 (see Results and Discussion).

Table 1. Crystal Data for [Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1) and [Pt(PPh3)(AuPPh3)(CuJ3)](NO3) (3)

<table>
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</tr>
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| R1 | 0.0688 | 0.117 |
| wR2 | 0.162 | 0.285 |

Solvant molecules not included. a R = Σ||Fo| - |Fcal|/Σ|Fo|; b wR2 = (Σw(Fo2 - Fc2)2/Σw(Fo2))1/2.

51.8 ppm with J(P-P)(doublet) = 388 Hz; doublet at δ 51.8 ppm with J(P-P)(doublet) = 266 Hz. It was shown by 31P COSY NMR spectroscopy that all these resonances belonged to the unknown product and that they were not coupled to that of 3 (see Results and Discussion).

Structure Determination of [Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1) and [Pt(PPh3)(AuPPh3)(CuJ3)](NO3) (3). Collection and Reduction of Crystallographic Data. Since single crystals decomposed very quickly upon removal from the solvent mixture, a crystal of 1 was mounted in a capillary together with a mixture of acetone and diethyl ether and a crystal of 3 was mounted in a capillary together with a mixture of dichloromethane and petroleum ether 40/80.

X-ray data were measured on a Nonius CAD4 diffractometer. For 3 14250 reflections (h: 0 to 17; k: 0 to 33; l: -22 to 22; 0 ≤ ϕ ≤ 20°) were measured with a maximum scan time of 20 s/reflect. This set contained only 2150 observed (|> 3σ(|)) reflections. All the reflections with a standard deviation of 1.5-4 σ(ι) were re-measured with a maximum scan time of 180 s/reflect. This resulted in 2306 reflections of which 1290 were "observed". These two sets for 3 were merged. Other standard experimental details for 1 and 3 are given elsewhere.12 Crystal data for 1 and 3 are given in Table 1.

Solution and Refinement of the Structures. [Pt(PPh3)(AuPPh3)(CuCl2PPh3)](NO3) (1). The positions of the metal atoms and ca. 80% of the phenyl carbon atoms were found from an automatic orientation and translation search (ORIENT12, TRACOR13) with a Au/Cl/Cu search model, followed by a phase refinement procedure to expand the fragment (DIRDIF14). The other phenyl rings and one NO3- were positioned from difference Fourier maps. The hydrogen atoms on the phenyl rings were placed at calculated positions (C-H = 0.93 Å). Of the unknown amount of solvent molecules none could be detected. An additional empirical absorption correction based on Fo = |F| was applied using DIFABS15 on the original unmerged Fo values.

The structure was refined by full-matrix least-squares on F2 values using SHELXL16 with anisotropic parameters for the metal, phosphorus, and chloride atoms and isotropic parameters for the carbon atoms. The NO3- ion and the phenyl rings were refined with constrained idealized geometry. The refinement converged at R = 0.068. The function minimized was Σω(Fo2 - Fc2)2 with w = 1/σ2(Fo) + (0.057F2)2. A maximum residual density of 1.4 e/Å3 was found near metal atoms.

The volume between the cluster molecules is 2280 Å3 (28 vol %) (PLATON17); this volume is filled with unidentified solvent molecules.

Selected bond distances and bond angles are given in Table 2. The molecular structure of 1 is given in Figure 1.18 [Pt(PPh3)(AuPPh3)(CuJ3)](NO3) (3). The positions of the metal atoms were found from automatic Patterson interpretation (PATTY19) followed by a phase refinement procedure to expand the fragment (DIRDIF14). The phenyl rings were positioned from successive difference Fourier maps. At this stage the NO3- ion has not been located, and of the unknown amount of solvent molecules none could be detected.

The phenyl rings were refined with constrained idealized geometry, with the hydrogen atoms placed at calculated positions (C-H = 0.93 Å). An additional empirical absorption correction based on Fo = |F| was applied using DIFABS15 on the original unmerged Fc values. The structure was refined by full-matrix least-squares on Fo values using SHELXL16 with anisotropic parameters for the metal, phosphorus, and iodine atoms and isotropic parameters for the carbon atoms. The refinement converged at R = 0.117. The function minimized was Σω(Fc2 - F2c2)2 with w = 1/σ2(Fc) + (0.114F2c2)2. The relatively large R value is caused by the disorder in the NO3- ions and the solvent molecules. A maximum residual density of 2.2 e/Å3 was found near metal atoms.

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Figure 1. X-ray structure of [Pt(PPh3)(AuPPh3)(CuCl3)PPh3] (NO3) (1) with atom labeling for Pt, Au, Cu, P, and Cl. Phenyl rings and the NO3- ion have been omitted for clarity. The thermal ellipsoids are at 50% probability.

The volume between the cluster molecules is 4065 Å³ (28 vol %) (PLATON); this volume is filled with unidentified solvent molecules with four NO3- ions per cell.

Selected bond distances and bond angles are given in Table 3.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for [Pt(PPh3)(AuPPh3)(CuCl3)] (NO3) (3)

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<tr>
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</tr>
<tr>
<td>Cu(4)–Au(16)</td>
<td>64.6(4)</td>
</tr>
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</table>

Cub distances to the phosphate-bonded Cu(1) (3.236–3.352 Å). These latter distances are comparable to Cu–Cu distances in e.g. [PPh3CuCl4]. The Cu–Cu distances, together with the Cu–Cl distances (Table 2), are such that Cu(1) can be viewed as pulled away from the Cu(2)–Cu(3)–Cu(4) triangle; this may be due to the coordination of the phosphate ligand to Cu(1). Support for this can be obtained from the related solid-state structure of 3 (vide infra).

The Pt–Cu distances and the Au–Cu distances to the copper atoms Cu(2), Cu(3), and Cu(4), together with the Pt–Au distances and the Au–Au distances, are all in the range normally observed.12,34–39 The Pt–Cu and Au–Cu bond lengths are smaller than the Pt–Au and Au–Au bond lengths, respectively (Table 2).

The AuPPh₃ groups, the platinum-bonded phosphine, and the Cu₄ unit surround the (central) platinum atom in a (quasi-)spheroidal symmetry, as indicated by the topological parameters $S$ and $P$,⁴⁰ which are 0.97 and 0.99, respectively. This spheroidal surrounding of the platinum atom is in accordance with the (S⁷P⁴⁵) ϵ-electron configuration (18 electrons) of 1 (the neutral fictitious Cu₄Cl₂P₃ entity is taken to donate one electron).

The presence of Cu–Cl stretching vibration of 1 is observed at 311 cm⁻¹. The solid-state structure as reported is in full agreement with the physical bulk data including elemental C, H, and N analysis and ICP analysis (see Experimental Section).

NMR Spectroscopy. The 3¹P NMR spectrum of 1 at room temperature (Figure 2A) shows resonances that can be assigned to the different phosphine sites as observed in the crystal structure of this cluster. This indicates that 1 shows no intramolecular fluxionality at room temperature and in contrast to the different phosphine sites as observed in the crystal structure analysis has also been evidenced by IR spectroscopy: the Cu–Cl stretching vibration of 1 is observed at 311 cm⁻¹. The solid-state structure as reported is in full agreement with the physical bulk data including elemental C, H, and N analysis and ICP analysis (see Experimental Section).

The six gold-bonded phosphines are all individually observed. Three sites are observed as three closely separated doublets near δ 52.3 ppm (sites B in Figure 2A) and three other closely separated doublets are found near δ 58.8 ppm (sites A in Figure 2A). Sites A and B correspond to the two AuPPh₃ triangles Au(2)–Au(3)–Au(4) and Au(5)–Au(6)–Au(7), respectively. The doublet nature of these sites is due to a $J(P–P)$ coupling of one phosphine site of the former AuPPh₃ triangle to one phosphine site of the latter AuPPh₃ triangle and vice versa as confirmed by the intense crosspeaks between sites A and sites B in the 3¹P COSY spectrum of 1 (Figure 2B).

From the doublet nature of sites A and B it can be concluded that the bonding in this cluster is primarily radial; in the case of strong peripheral interactions a triplet pattern for sites A and B would have been observed. The pattern of closely separated peaks for sites A and sites B is most likely not caused by such additional, small peripheral interactions because these peak positions were observed at constant chemical shifts using different field strengths, rather than that a constant peak separation on the frequency scale was observed. At room temperature a broad resonance can be observed near δ 5.0 ppm, i.e. these former two singlets together correspond to a total of one phosphine. This variable-temperature behavior is explained by a reversible dissociation–addition mechanism of the copper-bonded phosphine (P(8)); the singlet near δ –7.0 ppm originates from the copper-bonded phosphine ligand (P(1)) as evidenced by the value of the $J(P–^{195}Pt)$. Small spin–spin couplings between the platinum-bonded phosphine and the gold-bonded phosphines, although not detectable from the one-dimensional 3¹P NMR spectrum, are observed from the 3¹P COSY spectrum of 1 (Figure 2B; crosspeaks between sites A and C, and between sites B and C).

The AuPPh₃ groups, the platinum-bonded phosphine, and the Cu₄ unit surround the (central) platinum atom in a (quasi-)spheroidal symmetry, as indicated by the topological parameters $S$ and $P$,⁴⁰ which are 0.97 and 0.99, respectively. This spheroidal surrounding of the platinum atom is in accordance with the (S⁷P⁴⁵) ϵ-electron configuration (18 electrons) of 1 (the neutral fictitious Cu₄Cl₂P₃ entity is taken to donate one electron).
The temperature dependence of this equilibrium constant provides information on the enthalpy and entropy change for the phosphine dissociation of reaction 4: ΔH_diss ≈ +27 kJ·mol⁻¹ and ΔS_diss ≈ +88 J·mol⁻¹·K⁻¹ are estimated from the slope and the intercept of the lnK vs 1/T plot as −ΔH_diss/R and ΔS_diss/R, respectively. These values are in reasonable agreement with those that might be expected for a dissociation like reaction 4, therefore they provide additional support for the correctness of the proposed dissociation–addition mechanism.

The ¹⁹⁵Pt{¹H} NMR spectrum of 1 is observed at δ ~ 5761 ppm with a complex splitting pattern (Figure 4A), due to J couplings to the platinum-bonded and gold-bonded phosphines, that can be simulated with J(Pt–P)(doublet) = 2476 Hz, J(Pt–P)(quartet) = 358 Hz, and ³J(Pt–P)(quartet) = 450 Hz. Therefore the ¹⁹⁵Pt NMR coupling pattern is in agreement with the ³¹P NMR data and with the geometry of 1 as discussed above.

The ¹⁹⁵Pt NMR spectrum without proton decoupling is unchanged with respect to the ¹⁹⁵Pt{¹H} NMR spectrum. This shows that there is no hydride ligand present on 1.

Fast Atom Bombardment Mass Spectroscopy (FAB-MS). FAB-MS has been shown to be a successful technique for the determination of the correct molecular composition of cationic cluster compounds. The positive ion FAB-MS of 1 in the 2000–4000 mass range (Figure 5) has a large number of peaks; a selection of the centroids of heavy fragments as well as their assignments is given in Table 5. The result is in good agreement with the composition and the structure of 1 as discussed above.

No peaks with masses higher than that of M⁺ are observed. The relative abundance of the peak corresponding to the mass of M⁺ is very low, whereas that of (M – PPh₃)⁺ is more explicit. This might be related to the rather labile coordination of the copper-bonded phosphine as discussed above.

(a) Synthesis and Characterization of [Pt(PPh₃)(AuPPh₃)₆(Cu₄Br₃)](NO₃) (2) (y = 0 or 1). The reaction of [Pt(AuPPh₃)₆(NO₃)]²⁺ with [PPh₃CuBr]₄ in acetonitrile yields a mixture of compounds in which 2 is present in about 50%; several attempts to isolate 2 from this mixture were not successful. However, comparison of the ³¹P NMR data of compounds 1, 2, and 3 (vide infra), together with a comparison of the routes of synthesis of these three compounds, indicates 2 to be closely related to 1 and 3, respectively.

(b) Synthesis, Characterization, and Crystal Structure of [Pt(PPh₃)(AuPPh₃)₆(Cu₄Br₃)](NO₃) (3). When [Pt(AuPPh₃)₆(NO₃)]²⁺ is reacted with [PPh₃CuBr]₄ in acetonitrile, 3 is obtained. A single crystal of 3 could be obtained and an X-ray analysis of this crystal revealed the solid-state structure of 3. Cluster 3 was also characterized by ³¹P NMR spectroscopy and its presence was also confirmed by FAB-MS.

Since the red crystals, obtained by slow diffusion, all had the same morphology it is assumed that the solid consists of a single compound (3) of which the crystal structure will be reported below. However, the ³¹P NMR data show that in solution two rather similar compounds are present (3 and X, vide infra); since we were not able to separate these two
compounds or even to change their ratio, we believe that there is a simple chemical reaction converting 3 and X. Although no formulation of X can be given yet, we think that X most probably contains two Pt(AuPPh$_3$)$_3$ moieties.

**Crystal Structure.** The X-ray structure analysis, together with the $^{31}$P NMR data (vide infra), shows that the solid-state structure of 3 (Figure 6) is very similar to that of 1 (Figure 1), except for the copper-bonded phosphine which is missing in 3.

Table 6. $^{31}$P NMR Data for 1, 2, and 3

<table>
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<th>rel mass, m/e</th>
<th>% abundance</th>
<th>assignment</th>
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<tbody>
<tr>
<td>3310.6</td>
<td>100</td>
<td>(M - Cu - I + NO$_3^-$)</td>
</tr>
<tr>
<td>3260.1</td>
<td>200</td>
<td>(M - 2PPh$_3$)</td>
</tr>
<tr>
<td>3260.1</td>
<td>200</td>
<td>(M - 2PPh$_3$)</td>
</tr>
<tr>
<td>3260.1</td>
<td>200</td>
<td>(M - 2PPh$_3$)</td>
</tr>
</tbody>
</table>

*Not matched.*

Table 7. Positive Ion FAB-MS Data Corresponding to 3 (M$^+$ = [Pt(PPh$_3$)$_3$(CuI)$_3$](NO$_3^-$))

<table>
<thead>
<tr>
<th>rel mass, m/e</th>
<th>% abundance</th>
<th>assignment</th>
</tr>
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<tbody>
<tr>
<td>3718.8 3719.37</td>
<td>100</td>
<td>(M - Cu - I + NO$_3^-$)</td>
</tr>
<tr>
<td>3585.5 3585.52</td>
<td>66</td>
<td>(M - PPh$_3$)</td>
</tr>
<tr>
<td>3585.5 3585.52</td>
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<td>(M - PPh$_3$)</td>
</tr>
<tr>
<td>3585.5 3585.52</td>
<td>66</td>
<td>(M - PPh$_3$)</td>
</tr>
</tbody>
</table>

*Not matched.*

The six AuPPh$_3$ units are bonded to the (central) platinum atom in two layers which are arranged in a staggered way; a PPh$_3$ ligand is coordinated to this platinum atom. The CuI$_3$ unit consists of an almost ideal regular Cu$_4$ tetrahedron (Cu--Cu distances: 2.69--2.72 Å), in which three μ$_2$-I ligands are bridging the copper atoms; this Cu$_4$ tetrahedron is η$^2$ (face) bonded to the platinum atom through Cu(2), Cu(3), and Cu(4). However, short copper--gold and copper--platinum distances indicate that these copper atoms are part of the metal core. These three copper atoms, together with the six Au--P units, the Pt--P unit, and the three μ$_2$ halides, are arranged in a way that only slightly deviates from that in 1 (also see Tables 2 and 3). The only substantial difference between the solid-state structures of 1 (Figure 1) and 3 (Figure 6), apart from the absence of PPh$_3$ bonded to Cu(1) in 3, is that in 3 Cu(1) is situated more toward the Cu(2) face (Figure 6) in which the large iodide ligands in 3 prevent coordination of a PPh$_3$ ligand to Cu(1); even the smaller chloride ligands in 1 allow such phosphine coordination only when Cu(1) moves out of its "cuprophilic" pocket (see above). In this vision the solid-state structure of 3 can be regarded as representative of the structure of 1a; i.e.
Figure 7. $^3$P COSY NMR spectrum (202.462 MHz) at 298 K of the mixture containing [Pt(def)](AuPPh$_3$)$_2$(Cu$_3$)$_3$(NO$_2$)$_2$ (3) and the unknown product X (main peaks on the diagonal are labeled for these main peaks)* For coupling patterns compare to Figure 2B and see text.

after phosphine dissociation from 1, Cu(1) moves toward the Cu(2)–Cu(3)–Cu(4) triangle to result in 1a.

The large increase of the Cu–Cu(1) distances in going from the solid-state structures of 3 to 1 (Tables 3 and 2) implies that the bridging halides are vital in keeping the Cu$_3$ unit together.

The central platinum atom of 3, like that of 1, is surrounded in a (quasi-)spheroidal symmetry by the AuPPh$_3$ units, the platinum-bonded phosphine, and the Cu$_3$ unit. This classification is justified by the topological parameters $S$ and $P$, which amount to 0.97 and 0.99, respectively. This spheroidal surrounding is in agreement with the $(S)^2(P)^6$ electron configuration of 3.

**NMR Spectroscopy.** As for 1 and 2 the $^3$P NMR spectrum of 3 at room temperature is also indicative of a nonfluxional cluster compound. The platinum-bonded phosphine resonates at $\delta$ 36.2 ppm, and the gold-bonded phosphines are observed as two doublets; shoulders on these doublet peaks again indicate that these doublets are a result of closely separated signals. The coupling pattern and its interpretation are identical to those explained for 1 and 2. This was evidenced by the $^3$P COSY spectrum of 3 (Figure 7, peaks labeled with "3"), which shows a coupling pattern identical to that of 1 (Figure 2B).

From this $^3$P COSY spectrum it could be inferred that only one other (phosphorus-containing) compound (X) was present. The ratio of 3 to X is always ca. 1:5. Various attempts to separate 3 and X were unsuccessful. Some peaks of 3 and X are (partially) overlapping in the $^3$P NMR spectrum, but proper changing of spectrometer frequency, together with crosspeak analysis from the $^3$P COSY spectrum, provides clear insight in the coupling patterns of 3 and X (Figure 7). The coupling pattern of the unknown product X is largely similar to that of 1, 2, and 3, but it has an additional intense singlet at $\delta$ 51.8 ppm (for full $^3$P NMR data of the unknown product see the Experimental Section). This intense singlet proves that this signal does not belong to 3.

Variable-temperature $^3$P NMR experiments (295–213 K) did not reveal the presence of a copper-bonded phosphine as observed for 1. This is in agreement with the absence of such a phosphine in the solid-state structure of 3.

**Fast Atom Bombardment Mass Spectroscopy (FAB-MS).** A selection of the centroids of the heavy fragments (those being in agreement with the composition and structure of 3 as discussed above) as well as their assignments is given in Table 7. This FAB-MS shows several peaks where the NO$_3$ unit is still present in the molecular fragment, this in contrast to what is observed from the FAB-MS of 1. A tempting explanation for this difference is that in 3 the nitrate is somewhat more attracted to the cluster due to Cu(1), as compared to the situation in solid 1 where Cu(1) is shielded by coordination of a PPh$_3$.

Peaks with masses higher than M$^+$ are observed, but due to the possible presence of the unknown product X in the sample, or some minor contamination, nothing can be said about these peaks.

In this paper it was shown that the newly prepared compounds are Pt$\text{AuCu}_4$ clusters that can be regarded as Pt$\text{AuCu}$ and Cu$_3$ frames which have been fused together. The Cu$_3$X$_3$ moiety is recognizable as the metal halide frame of the parent cubane-like [PPh$_3$CuX]$_4$ (X = Cl, Br, I). We think this to be a strong indication that the cluster growth has occurred by merging the Cu$_3$ unit into the Pt$\text{AuCu}$ frame. The Pt takes the $\mu_2$ position over one of the Cu$_3$ faces replacing one of the halides, which has dissociated. To release steric strain two AuPPh$_3$ together with the copper-bonded phosphines dissociate, whereas the remaining halides take $\mu_2$ positions to reach a stable final product.

This view of cluster merging is additionally supported by reactions of clusters like [Pt(AuPPh$_3$)$_2$(NO)$_2$] with mononuclear metal compounds like Ag(PPh$_3$)(NO)$_3$ and CuCl: these reactions yield products in which the Ag or Cu atoms have been added to the cluster framework in non-adjacent positions.4–6

**Acknowledgment.** This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with fundamental support from the Netherlands Organization for the Advancement of Pure Research (NWO). Dr. M. F. J. Schoondergarg is thanked for his preliminary studies.6 We acknowledge Mrs. Véronique J. Zwikker and Mr. Roger A. J. M. Klaer for their contributions. Prof. L. H. Pignolet of the University of Minnesota is gratefully thanked for his fruitful discussions and for providing the opportunity to do FAB-MS experiments.

**Supporting Information Available:** A listing of crystallographic details and fractional positional parameters, anisotropic thermal parameters, and bond distances and angles (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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