This could be due to the presence of two facial PPh_3 ligands, which are expected to stabilize the lower oxidation state of the metal compared to hard-base N- and O-donor ligands. The Ru^{III}_2/$Ru^{II}Ru^{III}$ couple in **2** is found to be quasireversible while the same process in $[Ru_2O(O_2CMe)_2(py)_6]^{2+}$ and $[Ru_2O(O_2CMe)_2(Me_3tacn)_2]^{2+}$ is known[6,9] to be irreversible. Besides the PPh_3 ligands, the amidine functionality of the chelating ligand in **2** enhances the stability of the $Ru^{II}Ru^{III}$ mixed-valence state.

Discussion

The mechanism involved in the formation of the amino–amidine chelate rings in **2** from **1** by the nucleophilic attack of en to the MeCN facial ligands of **1** is an interesting aspect of this study. The amine–amidine chelate formation may take place by either of the two equally probable mechanistic pathways. In pathway a the reaction may proceed through an initial nucleophilic attack of en to the MeCN ligand cis to the μ-oxo ligand followed by a substitution of the trans MeCN ligand by the NH_2 group of en. Pathway b involves an initial substitution of the trans MeCN ligand by en followed by a nucleophilic attack of the free NH_2 group of the η^1-en to the cis MeCN ligand.

In the molecular structure of **1a**, the trans μ-oxo Ru–N bond length of 2.090 (6) Å is longer than the cis μ-oxo Ru–N distance of 2.048 (9) Å.[11] A substitution of the trans MeCN ligand is expected to be more facile than a substitution of the cis ligand. Again, due to the presence of strong interaction in the $\{Ru_2(\mu\text{-}O)^{4+}\}$ moiety, the extent of π-back-bonding from ruthenium to the nitrogen atom of MeCN will be more to the cis ligand than the trans ligand. This is reflected[11] in the C–N bond lengths of **1a**, which shows a longer C–N(cis) bond length compared to the C–N(trans) distance. The PPh_3 facial ligand in **1a** imposing steric constraints on the trans MeCN ligand in presence of two bridging O_2CAr ligands could facilitate a nucleophilic attack on the cis ligand. Structural data[11] on **1** thus clearly suggest a more favorable nucleophilic attack on the cis MeCN ligand than the trans one as is evidenced from the molecular structure and ^1H NMR spectral data of **2**.

Conclusions

A new diruthenium(III) complex, $[Ru_2O(O_2CAr)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2](ClO_4)_2$ (**2**), with an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2{}^{2+}\}$ core and two seven-membered amino–amidine chelate rings, formed by nucleophilic attacks of en to MeCN facial ligands in $[Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ (**1**), is isolated and characterized. The X-ray structure of **2c** shows that the nucleophilic attack takes place on the MeCN ligands, which are cis to the μ-oxo ligand in **1**. ^1H NMR spectral studies show a static conformation of the seven-membered chelate rings.

Visible spectral and electrochemical data show the effect of the facial ligands on the electronic structure and the stability of the diruthenium(III) core. The reduction couple Ru^{III}_2/$Ru^{II}Ru^{III}$ is found to be quasireversible. In the presence of an asymmetric chelating facial ligand, complex **2** exemplifies the first triply bridged diruthenium(III) complex with three facial sites on each ruthenium occupied by three donor atoms of different σ-donor and π-acceptor abilities, viz., PPh_3, N(amine), and N(amidine).

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Registry No. **1a**, 126948-63-8; **1a**$^{3+}$, 136804-65-4; **1b**, 136827-02-6; **1b**$^{3+}$, 136804-66-5; **1c**, 126980-10-7; **1c**$^{3+}$, 136804-67-6; **1d**, 136827-04-8; **2a**, 136804-69-8; **2b**, 136827-06-0; **2c**, 136804-72-3; **2d**, 136804-74-5; en, 107-15-3; MeCN, 75-05-8.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal data, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles for $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2](ClO_4)_2\cdot CH_2Cl_2\cdot 1.5H_2O$ (16 pages); a table of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Inorganic Chemistry and Crystallography
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Synthesis and Characterization of Copper- and Silver-Containing Platinum–Gold Cluster Compounds. X-ray Crystal Structure of $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2\cdot CH_3OH$

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The reactions of CuCl with $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(AuPPh_3)_8]^{2+}$ lead to the formation of $[Pt(CuCl)(AuPPh_3)_8]^{2+}$ (**1**) and $[Pt(CO)(CuCl)(AuPPh_3)_8]^{2+}$ (**2**), respectively. On addition of PPh_3 to a reaction mixture containing CuCl and $[Pt(CO)(AuPPh_3)_8]^{2+}$, two CuCl groups are incorporated, yielding $[Pt(CO)(CuCl)_2(AuPPh_3)_7]^{+}$ (**3**). A cluster with two Ag atoms, $[Pt(CO)(Ag)_2(AuPPh_3)_7]^{3+}$ (**4**), was obtained by treatment of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with 2 equiv of $Ag(PPh_3)NO_3$. The structure of **1** was determined by a single-crystal X-ray analysis. It crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 17.057$ (8) Å, $b = 16.260$ (2) Å, $c = 26.446$ (5) Å, $\alpha = 96.64$ (6)°, $\beta = 97.88$ (2)°, $\gamma = 78.10$ (6)°, and $V = 7080$ (4) Å^3 (Mo Kα radiation). The residuals are $R = 0.060$ and $R_w = 0.069$ for 8071 observed reflections and 460 variables. The probable presence of solvent molecules in the crystal was deduced from this structural analysis. The symmetry of the metal cluster is nearly C_s. The central Pt atom is surrounded by eight Au atoms and one Cu atom. A phosphine is attached to each of the Au atoms, and a Cl atom is attached to the Cu atom. Compared to its parent cluster $[Pt(AuPPh_3)_8]^{2+}$ the cluster has retained its electron count and toroidal geometry. The other PtCu compounds are assumed to contain Pt–Cu bonds as well. They were characterized by elemental analyses and by ^{31}P and ^{195}Pt NMR spectroscopic properties. The ^{195}Pt NMR spectrum of **3** gives evidence for the presence of two Pt–Ag bonds.

Introduction

Since several years, homonuclear gold clusters as well as heteronuclear metal–gold cluster compounds have been studied in our and other laboratories. Several papers and review articles on these clusters were published.[1-9] It is partly due to their potential of being homogeneous catalysts that they have gained such interest. However, up to now only a few have shown catalytic behavior.[10,11] To make metal–gold clusters more interesting from a catalytic point of view, other metal atoms were introduced.

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Recently clusters with different central atoms such as $[Rh(AuPPh_3)_6(AuCl)_2(CNC_8H_9)_2]^{2+}$[1] and $[Pd(AuPPh_3)_8]^{2+}$[2] and with other peripheral atoms such as $[Pt(Ag)(AuPPh_3)_8]^{3+}$,[3,4] $[Pt(H)(AuPPh_3)_7(SnCl_3)]^+$,[5] and $[Pt(HgNO_3)_2(AuPPh_3)_8]^{2+}$[3,6] have been reported. For some of these compounds the hydrogenation of 1-hexene has been studied. So far, they failed to give positive results.[5] The aim of our present investigations is to study the incorporation of Cu and Ag into the periphery of Pt–Au clusters.

Recently, Kanters et al. reported the addition of $AgNO_3$ to $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(AuPPh_3)_8]^{2+}$.[3,4] In these electrophilic additions the electron configurations of the clusters do not change.

$$[Pt(AuPPh_3)_8]^{2+} + Ag^+ \rightarrow [Pt(Ag)(AuPPh_3)_8]^{3+} \quad (1)$$

$$[Pt(CO)(AuPPh_3)_8]^{2+} + Ag^+ \rightarrow [Pt(CO)(Ag)(AuPPh_3)_8]^{3+} \quad (2)$$

In reaction 1 a Pt-centered product was formed with $(S^\sigma)^2(P^\sigma)^4$ configuration (6 valence electrons) and toroidal geometry. The CO adduct has spheroidal geometry with 8 electrons filled in cluster orbitals, $(S^\sigma)^2(P^\sigma)^6$.[4] When the 10 5d electrons of platinum are also taken into account, the similarity with the common electron count of 16 or 18 electrons in mononuclear platinum compounds is more obvious.

In 1989 Salter reviewed the heteronuclear cluster chemistry of copper, silver, and gold.[12] Only a few clusters were given in which copper atoms are connected to platinum by bridging ligands. In the literature, only a few compounds containing unbridged Pt–Cu bonds have been reported.[13-16] Recently, Espinet et al. described $[Pt_2Cu_4(C{\equiv}CR)_8]$ in which two acetylides are coordinated to each of the copper atoms.[17] However, the distances in the PtAg analogue between Pt and Ag are longer than 3.0 Å; therefore, it was concluded that the Pt–metal bonds are weak.

This paper deals with the incorporation of two Ag atoms and of one or two Cu atoms into $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(AuPPh_3)_8]^{2+}$. The products obtained were characterized by elemental analyses, by IR, ^{31}P NMR, and ^{195}Pt NMR spectroscopy, and by FAB-MS measurements. The crystal structure of $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2\cdot CH_3OH$ was determined by single-crystal X-ray analysis.

Experimental Section

Analyses and Physical Measurements. Analyses were carried out at the analytical laboratory of this university and at the Analytical Laboratory, Engelskirchen, FRG. ICP measurements in DMSO solutions were done on a Plasma 200 ICP-AE apparatus from Thermo Jarrell Ash to give Pt:Au:P:Cu (Ag) ratios. In the case of copper-containing clusters the intensity of the P line could not be determined because of overlap with a Cu line. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CPX-300 NMR spectrometer at 121.44 MHz and on a Bruker WM-200 spectrometer at 81.02 MHz in CH_2Cl_2 solutions and TMP (trimethyl phosphate) in CD_2Cl_2 as external reference. $^{195}Pt\{^1H\}$ NMR spectra and the $^{195}Pt\{^1H,^{31}P\}$ NMR spectrum were recorded on a Bruker WM-200 NMR spectrometer at 43.02 MHz in CD_2Cl_2 solutions with K_2PtCl_6 in D_2O as external reference.

The IR spectra of CsI pellets were recorded on a Perkin-Elmer 1720-X infrared Fourier transform spectrometer.

Fast atom bombardment mass spectroscopy (FAB-MS) measurements were carried out at the Mass Spectrometry Service Laboratory in the University of Minnesota, using a VG Analytical Ltd 7070 E-HF high-resolution double-focusing mass spectrometer, with a procedure as described elsewhere.[18]

Electrical conductivity measurements were performed with a Metrohm Konductoskop and a Philips PW 9510/00 conductivity cell.

Preparation of the Compounds. $[Pt(AuPPh_3)_8](NO_3)_2$,[19] $[Pt(CO)(AuPPh_3)_8](NO_3)_2$,[20] $[Pt(CO)(Ag)(AuPPh_3)_8](NO_3)_3$,[4] $Ag(PPh_3)(NO_3)$,[21] and CuCl[22] were synthesized according to the literature. All other reagents and solvents were commercially available and used without further purification.

$[Pt(CuCl)(AuPPh_3)_8](NO_3)_2$ (1). With stirring, 2.7 mg (0.027 mmol) of CuCl was added to a solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 30 mL of methanol at room temperature. Two days later, the solution was filtered and the filtrate was evaporated to dryness. The crude product was recrystallized by slow diffusion of diethyl ether in a methanol solution. Dark brown X-ray-quality crystals were isolated, washed with diethyl ether, and dried in vacuo. Yield: 60 mg (0.015 mmol). The crystals are soluble in dichloromethane, acetone, and alcohols and are insoluble in THF and diethyl ether.

Anal. Calcd for $Au_8CuPtP_8C_{144}H_{120}ClN_2O_6$ (M_r 4092.2): C, 42.27; H, 2.96; N, 0.68. Found: C, 40.53; H, 2.98; N, 0.72. ICP: Pt:Au:Cu = 1.0:8.0:1.1. IR: ν(uncoordinated NO_3^-) = 1346 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 56 ppm (s, b); $^2J_{Pt-P} = 4 \times 10^2$ Hz. $^{195}Pt\{^1H\}$ NMR: δ −4364.2 ppm (nonet); $^2J_{Pt-P}$ = 445 Hz. Equivalent conductance in acetonitrile at 25 °C: Λ_0 = 300 cm^2 Ω^{-1} mol^{-1}.

$[Pt(CO)(CuCl)(AuPPh_3)_8](NO_3)_2$ (2) was prepared in two ways.

Method A. A 100-mg (0.025-mmol) amount of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ and 2.7 mg (0.027 mmol) of CuCl were stirred together in methanol (30 mL) at room temperature. Two days later the solution was filtered and evaporated to dryness. Recrystallization by the slow diffusion of diethyl ether into a methanol solution yielded red crystals, which were washed with diethyl ether and dried in vacuo. Yield: 51 mg (0.012 mmol).

Method B. A dark brown solution of 100 mg (0.024 mmol) of $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2$ in dichloromethane almost immediately turned red when CO was bubbled through. The solvent was distilled off and the crude red product was dissolved in a minimal amount of methanol. Red crystals were obtained by the diffusion of diethyl ether into the red solution. Yield: 95 mg (0.023 mmol).

The crystals are soluble in dichloromethane, acetone, and alcohols and are insoluble in THF and diethyl ether.

Anal. Calcd for $Au_8CuPtP_8C_{145}H_{120}ClN_2O_7$ (M_r 4120.2): C, 42.27; H, 2.94; N, 0.68. Found: C, 41.93; H, 3.01; N, 0.73. ICP: Pt:Au:Cu = 1.0:8.2:1.0. IR: ν(CO) = 1958 cm^{-1}; ν(uncoordinated NO_3^-) = 1349 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 53.5 ppm (s); $^2J_{Pt-P}$ = 361 Hz. $^{195}Pt\{^1H\}$ NMR: δ −5737.7 ppm (nonet); $^2J_{Pt-P}$ = 361 Hz. Equivalent conductance in acetonitrile at 25 °C: 254 cm^2 Ω^{-1} mol^{-1}.

$[Pt(CO)(CuCl)_2(AuPPh_3)_7](NO_3)$ (3(NO$_3$)). Two methods can be used.

Method A. To a solution of 100 mg (0.025 mmol) of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ in 10 mL of dichloromethane were added 13.8 mg (0.053 mmol) of PPh_3 and 5.2 mg (0.053 mmol) of CuCl, and the solution was stirred for 24 h. Then it was filtered, and the filtrate was evaporated to dryness. The product was extracted by THF, whereafter the solvent was distilled off. The crude, red product was recrystallized from a dichloromethane–diethyl ether mixture (ratio approximately 1:3). Orange needles were filtered off, washed with diethyl ether, and dried in vacuo. Yield: 70 mg (0.019 mmol).

Method B. With stirring, 1 equiv of PPh_3 (6.4 mg, 0.024 mmol) and 1 equiv of CuCl (2.4 mg, 0.024 mmol) were added to a solution of 100 mg (0.024 mmol) of $[Pt(CO)(CuCl)(AuPPh_3)_8](NO_3)_2$ in 5 mL of dichloromethane. After the solution was stirred for 48 h at room tem-

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perature, the solvent was removed by distillation. Orange crystals were obtained as described above for method A. Yield: 80 mg (0.022 mmol).

The compound is soluble in dichloromethane, acetone, and THF, slightly soluble in alcohols, and insoluble in diethyl ether.

Anal. Calcd for $Au_7Cu_2PtP_7C_{127}H_{105}Cl_2NO_4$ (M_r 3697.9): C, 41.25; H, 2.86; N, 0.38; P, 5.86; Cu, 3.44. Found: C, 41.01; H, 2.99; N, 0.41; P, 5.80; Cu, 3.26. ICP: Pt:Au:Cu = 1.0:6.9:2.1. IR: ν(CO) = 1961 cm^{-1}; ν(uncoordinated NO_3^-) = 1353 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 55.3 ppm (s); $^2J_{Pt-P}$ = 377 Hz. $^{195}Pt\{^1H\}$ NMR: δ −5904.3 ppm; $^2J_{Pt-P}$ = 377 Hz. FABMS (*m*-nitrobenzyl alcohol matrix): m/z 3636 ($[Pt(CO)(CuCl)_2(AuPPh_3)_7]^+ = M^+$), 3608 ($(M - CO)^+$), 3537 ($(M - CuCl)^+$), 3346 ($(M - CO - PPh_3)^+$), 3083 ($(M - CO - 2PPh_3)^+$). Equivalent conductance in acetonitrile at 25 °C: 171 cm^2 Ω^{-1} mol^{-1}.

$[Pt(CO)(CuCl)_2(AuPPh_3)_7](PF_6)$ (3(PF_6)). An 18.6-mg (0.049-mmol) amount of $(C_4H_9)_4NPF_6$ in 3 mL of methanol was added to a solution of 30 mg (0.008 mmol) of $[Pt(CO)(CuCl)_2(AuPPh_3)_7](NO_3)$ in 20 mL of dichloromethane and stirred for 3 h. Then the solution was filtered. After evaporation to low volume diethyl ether was added to precipitate an orange-colored product. Orange crystals were obtained from a mixture of dichloromethane and diethyl ether. Yield: 27 mg (0.007 mmol).

Anal. Calcd for $Au_7Cu_2PtP_8C_{127}H_{105}Cl_2OF_6$ (M_r 3780.9): C, 40.35; H, 2.80. Found: C, 39.60; H, 2.91. ICP: Pt:Au:Cu = 1.0:6.9:2.1. IR: ν(CO) = 1961 cm^{-1}; $\nu(PF_6^-)$ = 840 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 55.3 ppm (s); $^2J_{Pt-P}$ = 377 Hz.

$[Pt(CO)(Ag)_2(AuPPh_3)_7](NO_3)_3$ (4) was prepared by two methods.

Method A. A 100-mg (0.024-mmol) sample of $[Pt(CO)(Ag)(AuPPh_3)_8](NO_3)_3$ was dissolved in 5 mL of dichloromethane. With stirring, 10.3 mg (0.024 mmol) of $Ag(PPh_3)(NO_3)$, dissolved in 2 mL of dichloromethane, was added slowly to the red solution. Upon addition the solution darkened immediately. After 1 h, the volume of the solution was reduced to 3 mL and diethyl ether was added until precipitation started. The solution was now allowed to stand overnight at room temperature. Dark red crystals were collected on a frit, washed with diethyl ether, and dried in vacuo. Yield: 35 mg (0.009 mmol).

Method B. A 21.6-mg (0.050-mmol) amount of $Ag(PPh_3)(NO_3)$ was added to a stirred red solution of 100 mg (0.025 mmol) of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ in 5 mL of dichloromethane. Upon addition the color changed to orange. Within a few minutes the solution darkened and the product was isolated as described under method A. Yield: 60 mg (0.016 mmol).

It is soluble in dichloromethane, alcohols, acetone, and THF but insoluble in diethyl ether.

Anal. Calcd for $Ag_2Au_7PtP_7C_{127}H_{105}N_3O_{10}$ (M_r 3839.6): C, 39.73; H, 2.76; N, 1.09. Found: C, 39.35; H, 2.80; N, 1.12. ICP: Pt:Au:Ag:P = 1.0:7.1:2.0:7.0. IR: ν(CO) = 1967 cm^{-1}; ν(coordinated NO_3^-) = 1285 cm^{-1}; ν(free NO_3^-) = 1356 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 58.0 ppm (t); $^3J_{Ag-P}$ = 17.4 Hz; $^2J_{Pt-P}$ = 395 Hz. $^{195}Pt\{^1H\}$ NMR: δ −5908.0 ppm (m); $^2J_{Pt-P}$ = 395 Hz; $^1J_{Pt-Ag} \approx$ 400 Hz. $^{195}Pt\{^1H, ^{31}P\}$ NMR: δ −5908.0 ppm (t, b); $^1J(^{109}Ag-^{195}Pt)$ = 415 Hz. Equivalent conductance in acetonitrile at 25 °C: 441 cm^2 Ω^{-1} mol^{-1}.

$[Pt(CO)(AgCl)_2(AuPPh_3)_7](NO_3)$ (5). With stirring, 2 equiv of LiCl (1.1 mg, 0.026 mmol) in methanol was added to a solution of 50 mg (0.013 mmol) of $[Pt(CO)(Ag)_2(AuPPh_3)_7](NO_3)_3$ in 2 mL of dichloromethane. Within 1 h orange crystals were formed. These crystals were collected on a frit and washed with methanol and diethyl ether. The product was dissolved in dichloromethane, the solution was filtered, and diethyl ether was added for crystallization. Yield: 40 mg (0.011 mmol).

The cluster is soluble in dichloromethane, acetone, and THF but insoluble in alcohols and diethyl ether.

Anal. Calcd for $Ag_2Au_7PtP_7C_{127}H_{105}NO_4Cl_2$ (M_r 3786.5): C, 40.28; H, 2.79; N, 0.37. Found: C, 40.23; H, 2.91; N, 0.41. IR: ν(CO) = 1962 cm^{-1}; ν(free NO_3^-) = 1348 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 56.4 ppm (t); $^3J_{Ag-P}$ = 15.8 Hz; $^2J_{Pt-P}$ = 395 Hz.

Structure Determination of $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2\cdot CH_3OH$ (1). Collection and Reduction of Crystallographic Data. Since the single crystals decomposed very quickly upon removal from the solvent mixture, a crystal of $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2\cdot CH_3OH$ was mounted in a capillary together with a mixture of methanol and diethyl ether. X-ray data were measured on an Enraf-Nonius CAD4 diffractometer. Standard experimental details, including the applied kind of absorption correction, are given elsewhere.[23] The crystal data are listed in Table I.

Table I. Crystal Data for $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2\cdot CH_3OH$

chem formula	$Au_8C_{145}ClCuH_{124}N_2O_7P_8Pt$	Z	2
mol wt	4124.2	space group	$P\bar{1}$ (No. 2)
a	17.057 (8) Å	T	20 °C
b	16.260 (2) Å	λ	0.71073 Å
c	26.446 (5) Å	ρ_{calc}	1.934 g/cm^3
α	96.64 (6) deg	μ(Mo Kα)	95.308 cm^{-1}
β	97.88 (2) deg	$R(F_o)^a$	0.060
γ	78.10 (6) deg	$R_w(F_o)^b$	0.069
V	7080 (4) Å^3		

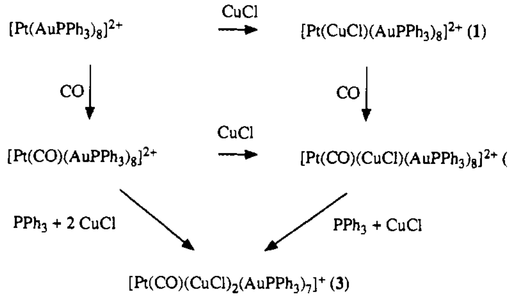
$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$.

Table II. Selected Fractional Positional and Thermal Parameters for $[Pt(CuCl)(AuP(C_6H_5)_3)_8](NO_3)_2$

atom	x	y	z	$100U_{eq}$,^{a} Å^2
Pt	0.32674 (7)	0.35639 (8)	0.26160 (5)	2.29 (5)
Au(1)	0.48454 (8)	0.31076 (9)	0.24972 (5)	3.43 (6)
Au(2)	0.36345 (8)	0.28269 (9)	0.16972 (5)	3.69 (6)
Au(3)	0.37749 (8)	0.44900 (9)	0.19999 (5)	3.64 (6)
Au(4)	0.17245 (8)	0.34979 (9)	0.26718 (5)	3.23 (6)
Au(5)	0.28526 (8)	0.35633 (9)	0.35630 (5)	3.11 (6)
Au(6)	0.39949 (8)	0.22084 (9)	0.30795 (5)	3.47 (6)
Au(7)	0.22011 (8)	0.41237 (9)	0.18272 (5)	3.24 (6)
Au(8)	0.22926 (8)	0.50080 (9)	0.28414 (5)	3.58 (6)
Cu	0.4335 (2)	0.3698 (2)	0.34093 (13)	1.81 (14)
P(1)	0.6188 (6)	0.2922 (7)	0.2390 (4)	5.5 (5)
P(2)	0.3638 (6)	0.1737 (6)	0.1066 (4)	4.7 (4)
P(3)	0.4190 (6)	0.5706 (6)	0.1892 (4)	4.4 (4)
P(4)	0.0587 (5)	0.2976 (6)	0.2701 (4)	4.0 (4)
P(5)	0.2624 (5)	0.3583 (6)	0.4411 (3)	3.4 (4)
P(6)	0.4502 (5)	0.0873 (6)	0.3302 (4)	3.7 (4)
P(7)	0.1321 (6)	0.4451 (6)	0.1111 (3)	4.0 (4)
P(8)	0.1916 (6)	0.6339 (6)	0.3204 (4)	4.0 (4)
Cl	0.5130 (6)	0.4158 (7)	0.4000 (4)	7.0 (5)

$^a U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

Scheme I. Routes To Synthesize **1–3**



Solution and Refinement of the Structure. The positions of the metal atoms were found from an orientation and translation search (ORIENT, TRACOR[24]) with an ideal Au_4 tetrahedron (Au–Au distance: 2.80 Å), followed by a phase refinement procedure to expand the fragment (DIRDIF[24]). The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The phenyl rings were converted into regular hexagons, and their hydrogen atoms were placed at ideal positions (C–H = 1 Å). A difference Fourier map showed the presence of one fully and two partially occupied NO_3^- ions. The latter were refined with a 0.5 occupancy factor and constrained ideal geometry. The spurious peaks around the partially occupied ions are presumably due to partially occupied methanol. The structure was refined by full-matrix least squares using SHELX.[24] During the final stage of the refinement, the anisotropic parameters of the gold, platinum, phosphorus, and chlorine atoms were refined. Final convergence was reached at $R = 0.060$; the function minimized was $\sum w(F_o - F_c)^2$ with $w = 2.4783/[\sigma^2(F_o) + 0.0005F_o^2]$. The maximum residual density was 1.3 e/Å^3 near the Pt and Au atoms. Further residual density was below 0.8 e/Å^3.

Positional and thermal parameters of selected atoms are given in Table II, and selected bond distances and angles are given in Table III. The molecular structure is given in Figure 1.[25]

Results

The routes to synthesize the newly reported clusters are outlined in Schemes I and II. The spectroscopic data of the discussed

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Scheme II. Routes To Synthesize **4**

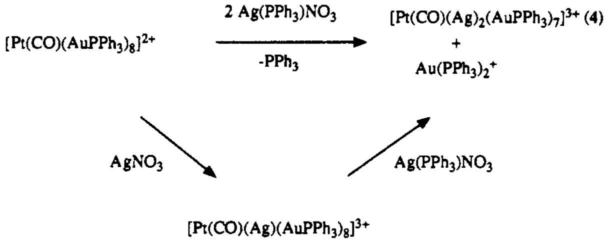

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Pt(CuCl)(AuP(C_6H_5)_3)_8](NO_3)_2$ (with Esd's)

Pt–Au(1)	2.692 (2)	Au(4)–Au(8)	2.789 (2)
Pt–Au(2)	2.677 (2)	Au(5)–Au(6)	2.924 (3)
Pt–Au(3)	2.676 (2)	Au(5)–Au(8)	3.112 (3)
Pt–Au(4)	2.681 (2)	Au(7)–Au(8)	2.893 (2)
Pt–Au(5)	2.694 (2)	Au(1)–Cu	2.682 (4)
Pt–Au(6)	2.642 (2)	Au(5)–Cu	2.671 (4)
Pt–Au(7)	2.684 (2)	Au(6)–Cu	2.629 (4)
Pt–Au(8)	2.640 (2)	Au(1)–P(1)	2.301 (10)
Pt–Cu	2.603 (4)	Au(2)–P(2)	2.289 (10)
Au(1)–Au(2)	2.814 (2)	Au(3)–P(3)	2.292 (11)
Au(1)–Au(3)	2.907 (3)	Au(4)–P(4)	2.286 (10)
Au(1)–Au(6)	2.936 (3)	Au(5)–P(5)	2.324 (9)
Au(2)–Au(3)	2.779 (2)	Au(6)–P(6)	2.278 (9)
Au(2)–Au(7)	2.912 (3)	Au(7)–P(7)	2.291 (8)
Au(3)–Au(7)	2.834 (3)	Au(8)–P(8)	2.266 (9)
Au(4)–Au(5)	2.838 (2)	Cu–Cl	2.098 (11)
Au(4)–Au(7)	2.837 (2)		
Au(1)–Pt–Au(2)	63.21 (10)	Au(5)–Pt–Au(7)	122.75 (14)
Au(1)–Pt–Au(3)	65.56 (12)	Au(5)–Pt–Au(8)	71.36 (11)
Au(1)–Pt–Au(4)	162.1 (2)	Au(7)–Pt–Au(8)	65.83 (9)
Au(1)–Pt–Au(5)	117.26 (13)	Au(6)–Pt–Au(7)	144.33 (16)
Au(1)–Pt–Au(6)	66.78 (13)	Au(6)–Pt–Au(8)	137.64 (8)
Au(1)–Pt–Au(7)	119.76 (10)	Au(1)–Pt–Cu	60.84 (13)
Au(1)–Pt–Au(8)	134.7 (2)	Au(2)–Pt–Cu	123.7 (2)
Au(2)–Pt–Au(3)	62.55 (10)	Au(3)–Pt–Cu	98.90 (16)
Au(2)–Pt–Au(4)	107.35 (11)	Au(4)–Pt–Cu	124.19 (12)
Au(2)–Pt–Au(5)	153.5 (2)	Au(6)–Pt–Cu	60.16 (14)
Au(2)–Pt–Au(6)	92.37 (11)	Au(5)–Pt–Cu	60.53 (11)
Au(2)–Pt–Au(7)	65.80 (9)	Au(7)–Pt–Cu	155.4 (2)
Au(2)–Pt–Au(8)	129.04 (9)	Au(8)–Pt–Cu	95.97 (14)
Au(3)–Pt–Au(4)	125.51 (11)	Pt–Au(1)–P(1)	171.7 (4)
Au(3)–Pt–Au(5)	143.62 (16)	Pt–Au(2)–P(2)	151.1 (3)
Au(3)–Pt–Au(6)	132.2 (2)	Pt–Au(3)–P(3)	148.7 (3)
Au(3)–Pt–Au(7)	63.83 (10)	Pt–Au(4)–P(4)	161.0 (3)
Au(3)–Pt–Au(8)	82.48 (12)	Pt–Au(5)–P(5)	174.3 (3)
Au(4)–Pt–Au(5)	63.73 (9)	Pt–Au(6)–P(6)	166.1 (3)
Au(4)–Pt–Au(6)	99.84 (16)	Pt–Au(7)–P(7)	173.6 (3)
Au(4)–Pt–Au(7)	63.85 (10)	Pt–Au(8)–P(8)	157.6 (3)
Au(4)–Pt–Au(8)	63.21 (15)	Pt–Cu–Cl	163.9 (4)
Au(5)–Pt–Au(6)	66.43 (11)		

compounds are given in the Experimental Section. Some IR (CO stretch vibrations), ^{31}P NMR, and ^{195}Pt NMR data are listed in Table IV. The $^{195}Pt\{^1H,^{31}P\}$ NMR spectrum of **4** is shown in Figure 2.

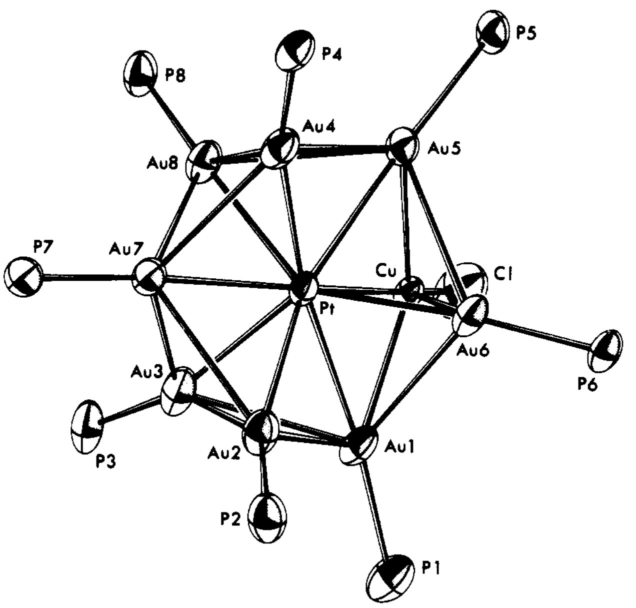

Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn with 50% probability boundaries. Phenyl rings have been omitted for the sake of clarity.

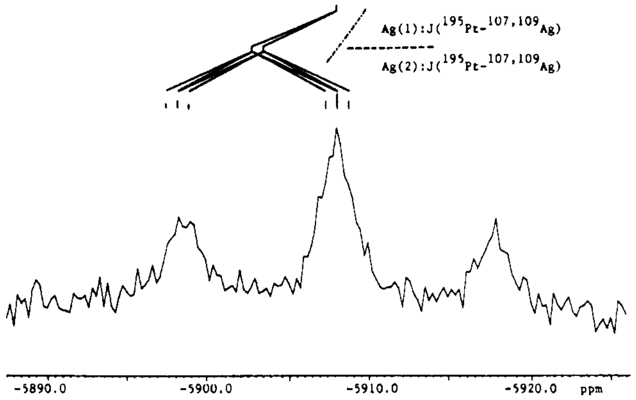

Figure 2. $^{195}Pt\{^1H,^{31}P\}$ NMR spectrum (CD_2Cl_2 solution with external $PtCl_6^{2-}$ standard) of $[Pt(CO)(Ag)_2(AuPPh_3)_7]^{3+}$ (**4**).

Discussion

Synthesis and Characterization of 1. $[Pt(Ag)(AuPPh_3)_8]^{3+}$ is described in previous reports.[3,4] We have shown now that, instead of $AgNO_3$, CuCl can also be used as a lewis acid in the reaction with $[Pt(AuPPh_3)_8]^{2+}$. When $[Pt(AuPPh_3)_8]^{2+}$ and CuCl are stirred together in methanol for a few days, **1** can be isolated. **1** was characterized by ICP and C, H, and N elemental analyses, IR and ^{31}P and ^{195}Pt NMR spectroscopy, and a solid-state structure determination. Elemental analyses reveal a composition analogous to $[Pt(Ag)(AuPPh_3)_8]^{3+}$ with Ag^+ substituted by CuCl: $[Pt(CuCl)(AuPPh_3)_8]^{2+}$. The IR spectrum agrees with the

Table IV. $^{31}P\{^1H\}$ NMR, $^{195}Pt\{^1H\}$ NMR, and IR Data for Cluster Compounds

	NMR			IR	
compd	$\delta(^{31}P)$, ppm	$\delta(^{195}Pt)$, ppm	$^2J_{Pt-P}$, Hz	$\nu(CO)$, cm^{-1}	ref
$[Pt(AuPPh_3)_8]^{2+}$	55.4	–4528.3	497		19
$[Pt(CO)(AuPPh_3)_8]^{2+}$	51.3	–5456.7	391	1940	20
$[Pt(CuCl)(AuPPh_3)_8]^{2+}$ (**1**)	56	–4364.2	445		this work
$[Pt(CO)(CuCl)(AuPPh_3)_8]^{2+}$ (**2**)	53.5	–5737.7	361	1958	this work
$[Pt(Ag)(AuPPh_3)_8]^{3+}$	57.0	–4376.2	453		4
$[Pt(AgCl)(AuPPh_3)_8]^{2+}$	56.5		453		*a*
$[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$	54.7	–5688.0	370	1964	4
$[Pt(CO)(AgCl)(AuPPh_3)_8]^{2+}$	54.0		370	1948	*a*
$[Pt(CO)(CuCl)_2(AuPPh_3)_7]^+$ (**3**)	55.3	–5904.3	377	1961	this work
$[Pt(CO)(Ag)_2(AuPPh_3)_7]^{3+}$ (**4**)	58.0	–5908.0	395	1967	this work
$[Pt(CO)(AgCl)_2(AuPPh_3)_7]^+$ (**5**)	56.4		395	1962	this work

[a] Kanters, R. P. F. Unpublished results.

presence of only free nitrate ions. The $^{31}P\{^1H\}$ NMR spectrum of **1** at room temperature shows a broad resonance at 56 ppm. The line width is about 150 Hz (Bruker WM 200 spectrometer, 81.02 MHz). The $^2J_{Pt-P}$ coupling constant cannot be assigned accurately. This broadening cannot unambiguously be assigned to quadrupolar effects; a comparable broadening of the resonance was also found for $[Pt(Ag)(AuPPh_3)_8]^{3+}$. It might also be caused by an exchange process that is slow on the NMR time scale. The ^{195}Pt NMR spectrum shows an odd multiplet with intensities confirming the presence of eight $AuPPh_3$ groups. This indicates that the platinum atom must be in the center surrounded by eight peripheral Au atoms. From this spectrum the $^2J_{Pt-P}$ coupling constant can be determined accurately. The decrease of the phosphorus to platinum coupling constant from 497 Hz in the parent compound to 445 Hz can be understood by realizing that the presence of one more bond with the same number of cluster valence electrons lowers the Pt–Au bond order. Compared to the parent cluster compound (see Table IV) the chemical $\delta(^{195}Pt)$ shift of −4364 ppm is shifted to higher frequency. This suggests less shielding of the platinum atom after introducing CuCl in the cluster. The same can be concluded from the downfield shift found for **1** in the ^{31}P NMR spectrum. All the data just given point to the cluster compound $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2$ with Pt in the center surrounded by eight $AuPPh_3$ groups and one CuCl group. This view is confirmed by the single-crystal X-ray analysis. The crystal structure is given in Figure 1. Selected interatomic distances and angles are summarized in Table III. The structure is analogous to that of $[Pt(Ag)(AuPPh_3)_8]^{3+}$ with nine metal atoms around the center. From the NMR study it is concluded that the central atom is Pt. The symmetry of the cluster is nearly C_s with a pseudo mirror plane through the atoms Cu, Au(6), Au(7), and Pt. The CuCl is positioned in such a way that it has a connectivity of four to other metal atoms like Au(2,3,4,6,8) and unlike Au(1,5,7), which are connected to five other metal atoms. The Pt–Cu distance is 2.603 (4) Å, and the Pt–Cu–Cl bond angle (163.9(4) Å) is not far from linearity. The bond length is about the same as found for $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5](BF_4)$[13] and for the sandwich cluster $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2](PF_6)$.[14] The eight $AuPPh_3$ groups are bonded to the central Pt with normal bond lengths (average 2.673 Å, range 2.640–2.694 Å). The Au–Au bond distances (average 2.881 Å, range 2.779–3.112 Å) and the Au–P bond distances (average 2.291 Å, range 2.27–2.32 Å) are within the range of values normally found for Pt–Au cluster compounds. The peripheral Au–Cu distances (average 2.661 Å, range 2.629–2.682 Å) are quite short when compared to the Au–Au (range 2.73–3.00 Å[4]) and Au–Ag (range 2.76–3.26 Å[4,26]) bond distances in other cluster compounds. Abu-Salah and co-workers reported a gold–copper cluster complex, $[Au_3Cu_2(C_2Ph)_6]^-$, with Au–Cu distances in the range 2.783–3.016 Å.[27] The pertinent sums of Pauling R_1 radii[28] are Pt–Cu = 2.47, Pt–Au = 2.64, Au–Au = 2.68, and Au–Cu = 2.51 Å. Regarding these data it can be concluded that particularly the radial bonding interactions Pt–Cu and Pt–Au in **1** are strong, which is in agreement with the general assumption that for the stability of these compounds the radial interactions predominate.[29] Another interesting point of comparison is the mean interatomic Au–Cu distance in the intermetallic compounds Au_3Cu of 2.65 Å and in AuCu of 2.72 Å,[30] which implicates Au and Cu to be in close contact in the cluster, contributing substantially to the stability.

Two free NO_3^- groups are present (analysis and IR data) so the cluster is a 2+ ion, having 16 cluster valence electrons, which predicts a toroidal rather than a spheroidal shaped metal frame. With the use of the topological program TORUS,[31] taking into account only the metal atoms, calculations indeed show a toroidal topology with $S = 0.45$ and $P = 0.95$; for $[Pt(Ag)(AuPPh_3)_8]^{3+}$, $S = 0.45$ and $P = 0.97$ were calculated.

The chemical shift in the ^{195}Pt NMR spectrum is in accord with a toroidal geometry, as can be concluded from Table IV. In ^{195}Pt NMR spectra, 18-electron clusters are found in the range −6800 to −4900 ppm, while known 16-electron clusters are found between −4600 and −4200 ppm (vs $PtCl_6^{2-}$ in D_2O); the $^{195}Pt-^{31}P$ coupling constants are also in well-separated domains.

Synthesis and Characterization of 2. $[Pt(CO)(CuCl)(AuPPh_3)_8]^{2+}$ can be prepared almost quantitatively by the exposure of a solution of $[Pt(CuCl)(AuPPh_3)_8]^{2+}$ in methanol to a CO atmosphere. **2** is also formed when $[Pt(CO)(AuPPh_3)_8]^{2+}$ is treated with 1 equiv of CuCl in methanol. The elemental analyses of the product support the composition of $PtAu_8Cu(PPh_3)_8(NO_3)_2$. The CO stretching frequency of 1958 cm^{-1} in the IR spectrum is consistent with a terminal metal carbonyl. Compared to the $\nu(CO)$ absorption found for $[Pt(CO)(AuPPh_3)_8]^{2+}$ (see Table IV) it is shifted to a higher wavenumber. The ^{31}P NMR spectrum of **2** consists of a single resonance at 53.5 ppm with ^{195}Pt satellites at 361 Hz. Owing to fluxional behavior in solution at room temperature, the phosphorus atoms on the peripheral metal atoms are all equivalent and yield a single peak in the NMR spectrum. The chemical shift is lowered from 56 to 53.5 ppm upon addition of CO to **1** as a result of electronic differences between 16- and 18-electron cluster compounds. The ^{195}Pt NMR spectrum shows an odd multiplet, which agrees with the presence of eight $AuPPh_3$ groups coordinated to a central platinum atom. Compared to that found for $[Pt(CO)(AuPPh_3)_8]^{2+}$ the coupling constant $^2J_{Pt-P}$ (361 Hz) is low. This might be due to the fact that one more bond has to be maintained with the same number of electrons. The resulting lower electron density on the platinum atom also causes the shift to a higher frequency of the CO stretch vibration. All spectroscopic data and the fact that **2** is formed quantitatively from **1** and CO point to a cluster ion $[Pt(CO)(CuCl)(AuPPh_3)_8]^{2+}$, which is very similar to the known silver analogue.

Synthesis and Characterization of 3. In order to incorporate more than one CuCl group in the clusters, 2 equiv of CuCl was added to $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(AuPPh_3)_8]^{2+}$. However, for unclear reasons, for $[Pt(AuPPh_3)_8]^{2+}$ this resulted in the formation of $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$, which has been fully characterized before.[32]

The reaction of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with 2 equiv of CuCl affords instable products which have not been identified yet. This reaction is still under investigation.

To create more space on the periphery of the metal frame, PPh_3 can be used as a $AuPPh_3^+$ scavenger to form $Au(PPh_3)_2^+$. PPh_3 has often been used to synthesize new clusters removing a $AuPPh_3$ unit from the cluster.[33] When $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(AuPPh_3)_8]^{2+}$ are treated with PPh_3, no products other than starting materials can be detected by ^{31}P NMR spectrometry. However, the reaction of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with CuCl and PPh_3 proceeds quickly and gives a cluster with a $PtCu_2Au_7$ core in high yield. The product, **3**(NO_3) has an elemental analysis (Pt, Au, Cu, C, H, N) in accord with the given composition. The analyses of **3**(PF_6) agree with the presence of one counterion. The molecular composition is confirmed by its FAB mass spectrum. The positive ion FAB mass spectrum consists of well-resolved peaks in the 1000–4000 u mass range. The formation pattern for **3** can easily be assigned (see Experimental Section). The $^{31}P\{^1H\}$ NMR spectrum shows a single resonance with a ^2J coupling constant to Pt. This suggests the coordination of the phosphines to the peripheral gold atoms. The number of gold–phosphines follows from the ^{195}Pt NMR spectrum. The spectrum clearly shows an even multiplet of sharp lines with intensities confirming the

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presence of seven $AuPPh_3$ groups. The IR spectrum of **3** has a CO stretching frequency of 1961 cm^{-1}, which is somewhat higher than that found for $[Pt(CO)(AuPPh_3)_8]^{2+}$ and $[Pt(CO)(CuCl)(AuPPh_3)_8]^{2+}$ (see Table IV). This can be attributed to a lowering of π back-donation as a result from the net electron-withdrawing effect by the addition of CuCl and the splitting off of a $AuPPh_3^+$ group. The chemical shifts found for **3** in the ^{31}P NMR spectrum (δ(AuP)) as well as in the ^{195}Pt NMR spectrum ($\delta(^{195}Pt)$) are shifted to higher frequencies when compared to those of $[Pt(CO)(AuPPh_3)_8]^{2+}$ and **2**. This can be ascribed to the deshielding of the Pt center on addition of CuCl, as stated earlier. All spectroscopic data point to a monopositive cluster molecule with Pt in the center. To this center one CO, two CuCl, and seven $AuPPh_3$ groups are attached.

The reaction of CuCl and PPh_3 with $[Pt(AuPPh_3)_8]^{2+}$ at 40 °C yielded $[Pt(CuCl)(AuPPh_3)_8]^{2+}$ as the only product. The proposed equilibrium (3) probably lies extremely to the left; therefore, no space is provided for a second CuCl to come in.

$$[Pt(AuPPh_3)_8]^{2+} + PPh_3 \rightleftarrows [Pt(AuPPh_3)_7]^{+} + Au(PPh_3)_2^{+} \tag{3}$$

Another restriction for the number of groups around the metal center is its electron count. Eighteen-electron clusters have a spheroidal geometry; however, in 16-electron clusters the groups should be arranged in a toroid around the metal center so that the number of groups is more limited.

Synthesis and Characterization of 4. Treatment of a dichloromethane solution of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with 2 equiv of $Ag(PPh_3)NO_3$ affords **4** in high yield. The ICP analysis (Pt:Au:Ag:P ratios) reveals a core of seven Au, two Ag, and one Pt with seven P atoms. The IR spectrum of **4** shows, beside at 1356 cm^{-1} for free NO_3^-, at 1285 cm^{-1} a fairly strong absorption that belongs to coordinated NO_3^-. This means that in the solid state NO_3^- ions are coordinated to the Ag atoms. The conductivity measurements in acetonitrile indicate a 1:3 electrolyte. This suggests that in solution the nitrate ions are not coordinated but are free as was found before for $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$.[4] When the nitrate ions are substituted by chloride ions, the compound turns out to be insoluble in alcohols. This reflects the change to a less positive cluster, $[Pt(CO)(AgCl)_2(AuPPh_3)_7]^+$ (**5**). The resonance in the $^{31}P\{^1H\}$ NMR spectrum for **5** is found at a lower frequency than found for **4** in accord with increased electron density around P when Cl^- is coordinated to Ag^+. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a triplet (relative intensities 1:2:1, $^3J_{Ag-P}$ = 17.5 Hz) with Pt satellites at 395 Hz. The coupling constant of 395 Hz can be attributed to a $^2J_{Pt-P}$ coupling (normal range: 350–500 Hz), which indicates that Pt must be the central atom. Two silver atoms, directly attached to the Pt center, give rise to the triplet nature of the resonance. This view is confirmed by the $^{195}Pt\{^1H\}$ NMR spectrum, which consists of an even number of broad lines. The phosphorus atoms on the peripheral gold atoms split the ^{195}Pt resonance in eight lines ($^2J_{Pt-P}$ = 395 Hz), which are then split by two Ag atoms (consisting of 51.8% ^{107}Ag and 48.2% ^{109}Ag, both $I = {}^1/_2$) to yield a complicated pattern of resonances. The intensities of the lines suggest $^{195}Pt–^{109,107}Ag$ coupling constants that are of about the same magnitude as the $^{195}Pt–^{31}P$ coupling constant (ca. 400 Hz). The $^{195}Pt\{^1H,^{31}P\}$ NMR spectrum shows a triplet, which is direct evidence for the presence of two Ag atoms (see Figure 2). Separate $^{195}Pt–^{107}Ag$ and $^{195}Pt–^{109}Ag$ coupling constants could not be resolved; the average Pt–Ag coupling constant is 415 Hz.

All spectroscopic data agree with the proposed formulation of $[Pt(CO)(Ag)_2(AuPPh_3)_7](NO_3)_3$.

It would be of interest to find out whether the two Cu or Ag atoms in the metal frame are adjacent, as is found in most M_2Ru_x (M = Cu, Ag, Au; x = 4–6) clusters,[12,34] or not. Unfortunately, thus far no single crystals of **3** or **4** could be obtained, maybe due to the simultaneous crystallization of different isomers. Further study is in progress.

Acknowledgment. We thank Dr. E. A. Larka from the University of Minnesota for the FAB-MS measurements. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO).

Registry No. 1, 137040-36-9; **2**, 137040-38-1; $[Pt(AuPPh_3)_8](NO_3)_2$, 110870-05-8; $[Pt(CO)(AuPPh_3)_8](NO_3)_2$, 116887-03-7; $[Pt(CO)(Ag)(AuPPh_3)_8](NO_3)_3$, 124421-52-9; $Ag(PPh_3)(NO_3)$, 78514-14-4; ^{195}Pt, 14191-88-9; Cu, 7440-50-8; Pt, 7440-06-4; Au, 7440-57-5; Ag, 7440-22-4.

Supplementary Material Available: Tables of crystallographic details and additional temperature factors, fractional positional parameters, thermal parameters, and bond distances and angles (11 pages); a listing of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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