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Cluster Growth: Some Representative Reactions. Crystal Structures of $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ and $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$

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The reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $AgNO_3$ under H_2-atmosphere yields two new hydride-containing Pt−Au−Ag cluster compounds: $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (**1**) and $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**2**). These reactions show intimate details on cluster growth: the nine-metal-atom particle $[Pt(AuPPh_3)_8](NO_3)_2$ grows via oxidative addition of H_2, deprotonation and electrophilic addition of Ag^+ to a 10- and then to an 11-metal-atom particle, **2**. Cluster compounds **1** and **2** were characterized by elemental analyses, ICP analyses, IR and NMR (^1H, ^{31}P and ^{195}Pt) spectroscopy, and electrical conductivity measurements. The crystal and molecular structures of **1** and **2** have been determined by means of single-crystal X-ray analyses. The compound $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ crystallizes in space group $P2_1$, with $Z = 2$, $a = 15.475(7)$ Å, $b = 26.048(2)$ Å, $c = 16.586(2)$ Å, $\beta = 97.00(4)°$, and $V = 6636$ Å^3. Mo Kα radiation was used. The residuals are $R = 0.070$ and $wR_2 = 0.170$ for 6294 observed reflections and 311 variables. The compound $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ crystallizes in space group $P\bar{1}$ in two almost identical modifications. During X-ray measurement the first modification converted into the second modification, with a small loss of crystal solvent molecules. The X-ray analysis of the first modification revealed $Z = 2$, $a = 16.956(3)$ Å, $b = 17.48(1)$ Å, $c = 27.36(2)$ Å, $\alpha = 93.68(8)°$, $\beta = 97.55(4)°$, $\gamma = 76.16(8)°$, and $V = 7802$ Å^3; Mo Kα radiation was used. The residuals are $R = 0.055$ and $wR_2 = 0.151$ for 4169 observed reflections and 443 variables. The X-ray analysis of the second modification revealed $Z = 2$, $a = 16.848(4)$ Å, $b = 17.51(4)$ Å, $c = 27.40(3)$ Å, $\alpha = 96.3(2)°$, $\beta = 95.9(1)°$, $\gamma = 72.46(7)°$, and $V = 7639$ Å^3. Mo Kα radiation was used; the residuals are $R = 0.090$ and $wR_2 = 0.230$ for 5040 observed reflections and 443 variables. Both clusters, **1** and **2**, have a central Pt atom surrounded by eight Au and one (for **1**) or two (for **2**) Ag atoms; the Au atoms are attached to PPh_3 ligands, and the Ag atoms are coordinated to nitrate. In the $PtAgAu_8$ and the Pt Ag_2Au_8 frames, the hydride-ligand is positioned between Pt and Au and is located "trans" to the silver atoms. $[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$ and $[Pt(H)(AgCl)_2(AuPPh_3)_8](NO_3)$ can be regarded as the Cl-analogues of **1** and **2** respectively. $[Pt(H)(AuPPh_3)_8]^+$ (**3**) has been prepared by deprotonation of the dihydride cluster $[Pt(H)_2(AuPPh_3)_8]^{2+}$ using a basic solvent like pyridine.

Introduction

It is known from mixed metal−gold cluster chemistry that cluster growth often takes place by means of electrophilic addition of M^+ units (M = Au,[3,4] Ag,[5,6] Cu[7]). Another important pattern is oxidative addition of H_2 followed by electrophilic substitution of H^+ by Au(I) cations. Considerations of this kind have recently led to a large number of new cluster compounds, among which is the platinum−gold cluster $[Pt(AuPPh_3)_8]^{2+}$;[8] this cluster has a central platinum atom surrounded by eight $AuPPh_3$ groups. The proposed mechanism of formation of this cluster compound[9] is supported by independent full characterization of several of the proposed intermediates.[10,11] The $(S^\sigma)^2(P^\sigma)^4$ (16-electron) cluster compound $[Pt(AuPPh_3)_8]^{2+}$ reacts rapidly and fully reversibly with dihydrogen at ambient pressures and temperatures to give the $(S^\sigma)^2(P^\sigma)^6$ (18-electron) dihydride $[Pt(H)_2(AuPPh_3)_8]^{2+}$.[12]

This dihydride gives rise to new cluster compounds through electrophilic substitutions and electrophilic additions of Ag(I), Cu(I) and Au(I) units.[13] In this paper we report two new hydride containing PtAuAg-clusters prepared in this way: $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (**1**) and $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**2**). These two trimetallic $(S^\sigma)^2(P^\sigma)^6$ (18-electron) clusters are very active catalysts in $H_2{-}D_2$ equilibration reactions.[14] We also report the formation of $[Pt(H)(AuPPh_3)_8]^+$ (**3**) by depro-

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tonation of the dihydride using a basic solvent like pyridine. These reactions can be seen as important representative steps with respect to cluster growth mechanisms.

A large variety of heterometallic hydrido compounds containing gold (or silver) is known from the literature. The presence of hydride-bridges between the gold (or silver) and the heterometal-atom in these compounds is well-established either from direct or indirect observation by X-ray diffraction,[15-18] by spectroscopic data,[19] or from potential energy calculations.[16,17]

In a few cases terminal hydrides were observed in the solid state structures of aforementioned heterometallic compounds; the structures of these compounds in solution, however, often show the presence of bridging hydride ligands.[19,20]

Experimental Section

Measurements. Elemental analyses were carried out at the microanalytical department of the University of Nijmegen. ICP analyses, giving Pt:Au:Ag:P ratios, were carried out on a Plasma 200 ICP-AE spectrometer in DMSO solutions of the cluster compounds with $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$[6] and $[Pt(PPh_3)(AgNO_3)_3(AuPPh_3)_6]$[21] used for calibration.

$^{31}P\{^1H\}$ NMR spectra of CH_2Cl_2 (or CH_3OH) solutions were recorded on a Bruker WM-200 spectrometer operating at 81.015 MHz, on a Bruker CXP-300 spectrometer at 121.442 MHz, and on a Bruker AM-500 spectrometer operating at 202.462 MHz with trimethylphosphate (TMP) in CD_2Cl_2 (or CD_3OD) as external reference; ^1H NMR spectra were recorded in CD_2Cl_2 solutions on a Bruker WM-200 spectrometer operating at 200.13 MHz with tetramethylsilane (TMS) as reference. The ^{195}Pt NMR spectra were recorded at 43.02 MHz on a Bruker WM-200 spectrometer in CD_2Cl_2 solutions with K_2PtCl_6 in D_2O as external reference (for reasons of stability the ^{195}Pt NMR spectra of $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**2**) were accumulated under dihydrogen atmosphere). Phosphorus decoupling during ^{195}Pt NMR experiments was performed with a PTS 200 synthesizer. The infrared (IR) spectra of solid samples were measured in CsI pellets on a Perkin-Elmer 1720-X Fourier transform infrared spectrometer; solution IR spectra were taken from CH_2Cl_2 solutions between NaCl crystals. Electrical conductivity measurements were performed on a Metrohm E365B Konduktoskop with the use of a Unicam Pt-electrode conductivity cell. Acidimetric titrations to determine the number of released protons were carried out in methanol−water mixtures using aqueous NaOH solutions as titrant; the equivalence point was determined with a pH-sensitive electrode.

Preparations. $[Pt(AuPPh_3)_8](NO_3)_2$ and $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ were prepared according to literature methods.[9,6] This is also the case for $Ag(PPh_3)(NO_3)$ and $[Ag(PPh_3)Cl]_4$.[22] All solvents were of reagent grade and were used without further purification, except for those used in the synthesis of $[Pt(H)(AuPPh_3)_8](NO_3)$ (**3**) which were purified according to literature prescriptions.[23]

$[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (1). (A) An 80-mg (0.020-mmol) sample of $[Pt(AuPPh_3)_8](NO_3)_2$ was dissolved in 7 mL of methanol. Dihydrogen was bubbled through this solution for 15 min upon which the color changed from brown to red-brown; 2 mL of methanol, in which 4.0 mg (0.024 mmol) of $AgNO_3$ was dissolved, was subsequently added under dihydrogen atmosphere. After 5 h of stirring the color of the reaction mixture had changed from red-brown to deep red; the dihydrogen atmosphere was replaced by air, and the volume of the reaction mixture was reduced to 50% by evaporation under reduced pressure. Cluster **1** was precipitated as an orange-red powder by addition of diethyl ether (yield: 52 mg, 0.013 mmol; 65%, calculated for Pt).

(B) A 50-mg (0.012-mmol) sample of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ was dissolved in 30 mL of methanol; 500 mg (8.9 mmol) KOH was added to this brown solution under vigorous stirring. After the KOH was dissolved the volume of the red solution was reduced to 10 mL and a red precipitate was obtained by adding 40 mL of water. This precipitate was then filtered off. This red solid **1** was washed twice with 50 mL of water and finally with 20 mL of diethyl ether (yield: 44 mg, 0.011 mmol; 90%, calculated for Pt).

(C) A 50-mg (0.012-mmol) sample of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ was dissolved in 5 mL of dichloromethane (or methanol). Dihydrogen was bubbled through this solution for 15 min while the color of the reaction mixture changed from brown to red. The reaction vessel was then closed under dihydrogen atmosphere. After 1 h the vessel was opened to air, and the solution was evaporated under reduced pressure to a volume of 1 mL. A red precipitate, obtained upon addition of diethyl ether to this solution, was filtered off and washed with water and diethyl ether. Red crystals of $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ were obtained by slow diffusion of diethyl ether in a methanol solution of the sample (yield: 45 mg, 0.011 mmol; 91%, calculated for Pt).

Anal. Calcd for $PtAu_8AgP_8C_{144}H_{121}N_2O_6$ (mol wt 4102.02): C, 42.16; H, 2.97; N, 0.68. Found: C, 42.04; H, 3.04; N, 0.70. ICP: Pt:Au:Ag:P = 1:8.0:1.0:7.9. IR(solid): in addition to several absorption bands characteristic for the PPh_3 ligands, only bands at 1351 cm^{-1} (broad), originating from uncoordinated NO_3, and at 1292 cm^{-1} from coordinated NO_3 could be observed. IR(solution): only absorption bands from PPh_3 and uncoordinated NO_3 were present. ^{31}P NMR (CH_3OH): $\delta = 56.2$ ppm with $^2J(P-^{195}Pt)$ (doublet) = 410 Hz and $^3J(P-Ag)$ (doublet) = 21 Hz. ^{31}P NMR (CH_2Cl_2): $\delta = 54.7$ ppm with $^2J(P-^{195}Pt)$ (doublet) = 412 Hz and $^3J(P-Ag)$ (doublet) = 19 Hz. ^1H NMR (hydride): $\delta = +1.74$ ppm with $^2J(H-Ag)$ (doublet) = 19.7 Hz and $^3J(H-^{31}P)$ (nonet) = 12.5 Hz; $^1J(H-^{195}Pt)$ could not be observed due to the low *S/N* ratio of this hydride signal. ^{195}Pt NMR: $\delta = -6036.0$ ppm with $^1J(Pt-^1H)$ (doublet) = 716 Hz, $^1J(Pt-^{109}Ag)$ (doublet) = 487 Hz, $^1J(Pt-^{107}Ag)$ (doublet) = 425 Hz and $^2J(Pt-^{31}P)$ (nonet) = 412 Hz. Conductivity in methanol at 25 °C: $\Lambda_m{}^O = 224$ $S{\cdot}cm^2{\cdot}mol^{-1}$. Precipitation of **1** from the methanol solution of synthesis C with water instead of with diethyl ether and subsequent acidimetric titration of this methanol−water mixture revealed the presence of one released proton per Pt (see Results and Discussion); additional experiments showed that **1** is stable with respect to water.

$[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$. To a brown solution of 50 mg (0.012 mmol) of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ in 30 mL of methanol, 500 mg (8.9 mmol) of KOH was added. This mixture was stirred until all the KOH was dissolved. The solution was then evaporated to dryness under reduced pressure. The red solid was purified by solving it in 20 mL of dichloromethane and filtrating a white residue after which the red filtrate was evaporated to dryness under reduced pressure; this procedure was repeated three times. The red solid was then dissolved in 2 mL of dichloromethane, and 50 mg (0.13 mmol) tetra-*n*-butylammoniumhexafluorophosphate was added. After the mixture was stirred for 15 min, 25 mL of methanol was added and the solution was evaporated until a red precipitate was observed. The red solid $[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$ was filtered off and washed with methanol and diethyl ether (yield: 39 mg, 0.0094 mmol; 78%, calculated for Pt).

ICP analysis: Pt:Au:Ag:P = 1:8.1:1.0:8.1. The IR spectrum (CsI) shows a band at 258 cm^{-1}, tentatively assigned to the Ag−Cl stretching vibration, a band at 840 cm^{-1} originating from PF_6^- and several absorption bands characteristic for the PPh_3 ligands; no bands originating from coordinated or uncoordinated NO_3 could be observed. ^{31}P NMR (CH_3OH): $\delta = 55.3$ ppmwith $^2J(P-^{195}Pt)$ (doublet) = 414 Hz and

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^3J(P–Ag) (doublet) = 18 Hz. ^{31}P NMR (CH_2Cl_2): $\delta = 54.0$ ppm with ^2J(P–^{195}Pt) (doublet) = 411 Hz and ^3J(P–Ag) (doublet) = 17 Hz.

[Pt(H)(AgNO$_3$)$_2$(AuPPh$_3$)$_8$](NO$_3$) (2). (A) To a solution of [Pt(H)(AgNO$_3$)(AuPPh$_3$)$_8$](NO$_3$) (**1**) (50 mg, 0.012 mmol) in 7 mL of methanol, a solution of 2.6 mg (0.015 mmol) $AgNO_3$ in 1 mL of methanol was added dropwise. This mixture was stirred for 2 h while the color changed from deep red to dark red. The solution was then partially evaporated and a red precipitate was obtained by addition of diethyl ether. The red solid **2** was filtered off and washed with 20 mL of water and 15 mL of diethyl ether (yield: 43 mg, 0.010 mmol; 84%, calculated for Pt).

(B) An 8.3-mg (0.049-mmol) sample of $AgNO_3$ was dried in vacuum (10^{-3} mbar) for 2 h and subsequently dissolved in 1 mL of dried acetonitrile under inert nitrogen atmosphere. This was then added to a solution of 80 mg (0.020 mmol) [Pt(H)(AuPPh$_3$)$_8$](NO$_3$) (which was prepared according to the method described in this paper, vide infra) in 5 mL of dried dichloromethane. This solution was stirred for 2 h under a nitrogen atmosphere, because of the sensitivity of [Pt(H)(AuPPh$_3$)$_8$](NO$_3$) toward moisture and air. The solution was then evaporated to dryness under reduced pressure, and a brownish-red powder was obtained. The ^{31}P NMR (CH_2Cl_2) of this powder in air revealed the presence of **2** among [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$ and [Pt(AgNO$_3$)(AuPPh$_3$)$_8$](NO$_3$)$_2$ in about 50% yield (attempts to separate this mixture were not made).

(C) Dihydrogen was bubbled through a solution of [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$ (100 mg, 0.025 mmol) in 10 mL of methanol for 5 min; after this 8.5 mg (0.050 mmol) of $AgNO_3$ was added while stirring. Dihydrogen was bubbled through for 10 min more. The reaction vessel was then closed under a dihydrogen atmosphere, and the mixture was stirred for 1 h. The red solution was evaporated to dryness; the dark red powder was washed with water and diethyl ether. Dark red crystals of [Pt(H)(AgNO$_3$)$_2$(AuPPh$_3$)$_8$](NO$_3$) were obtained by slow diffusion of diethyl ether in a methanol solution of the product (yield: 102 mg, 0.024 mmol; 96%, calculated for Pt).

Anal. Calcd for $PtAu_8Ag_2P_8C_{144}H_{121}N_3O_9$ (mol wt 4271.90): C, 40.49; H, 2.85; N, 0.98. Found: C, 40.32; H, 2.89; N, 1.02. ICP: Pt:Au:Ag:P = 1:8.0:2.1:7.9. IR (solid): bands at 1346 cm^{-1} (broad), originating from uncoordinated NO_3 and at 1286 cm^{-1} from coordinated NO_3; several bands characteristic for the PPh_3 ligands. IR (solution): in addition to the bands from the PPh_3 ligands, a band at 1351 cm^{-1} (broad) from uncoordinated NO_3 and a band at 1295 cm^{-1}, originating from coordinated NO_3, could be observed; the relative intensity of the band from coordinated NO_3 was roughly halved with respect to the IR spectrum of the solid sample. ^{31}P NMR (CH_3OH): $\delta = 60.0$ ppm with ^2J(P–^{195}Pt) (doublet) = 406 Hz and ^3J(P–Ag) (triplet) = 20 Hz. ^{31}P NMR (CH_2Cl_2): $\delta = 58.6$ ppm with ^2J(P–^{195}Pt) (doublet) = 407 Hz and ^3J(P–Ag) (triplet) = 19 Hz. ^{195}Pt NMR: $\delta = -6347.6$ ppm with ^1J(Pt–^{1}H) (doublet) = 611 Hz, ^1J(Pt–^{109}Ag) (triplet) = 465 Hz, ^1J(Pt–^{107}Ag) (triplet) = 405 Hz and ^2J(Pt–^{31}P) (nonet) = 407 Hz. Conductivity in methanol at 25 °C: $\Lambda_m{}^O = 195$ S·cm^2·mol^{-1}. Precipitation of **2** in the methanol reaction mixture of synthesis route C with water (instead of evaporating the solution to dryness) and subsequent acidimetric titration of this methanol–water mixture (after additional experiments showed that **2** remained intact by this treatment) revealed the presence of one released proton per Pt (see Results and Discussion).

[Pt(H)(AgCl)$_2$(AuPPh$_3$)$_8$](NO$_3$). Dihydrogen was bubbled through a solution of 100 mg (0.025 mmol) of [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$ in 10 mL of dichloromethane for several minutes, upon which a slight change in color from brown to red-brown was observed. A 20.3-mg (0.0125-mmol) sample of [Ag(PPh$_3$)Cl]$_4$ was added and the reaction mixture was stirred under dihydrogen atmosphere for 6 h. The color gradually changed to deep red. The flask was then opened to air, and the mixture was filtered to remove minor amounts of metallic contaminations. The red filtrate was evaporated to dryness under reduced pressure. Deep red crystals of [Pt(H)(AgCl)$_2$(AuPPh$_3$)$_8$](NO$_3$) were obtained by slow diffusion of diethyl ether in a methanol solution of the sample (yield: 72 mg, 0.017 mmol; 68%, calculated for Pt).

ICP analysis: Pt:Au:Ag:P = 1:7.9:2.0:7.9. IR (solid): in addition to the bands from the PPh_3 ligands only absorption bands for uncoordinated NO_3 (1349 cm^{-1}, broad) and for the Ag–Cl stretching vibration (257 cm^{-1}) were observed. ^{31}P NMR (CH_2Cl_2): $\delta = 57.6$ ppm with ^2J(P–^{195}Pt) (doublet) = 406 Hz and ^3J(P–Ag) (triplet) = 16 Hz. Conductivity in methanol at 25 °C: $\Lambda_m{}^O = 93$ S·cm^2·mol^{-1}. When 100 mg (0.024 mmol) of [Pt(H)(AgNO$_3$)$_2$(AuPPh$_3$)$_8$](NO$_3$) was dissolved in methanol and 3 mg (0.07 mmol) of LiCl was added with subsequent stirring for 3 h, the ^{31}P NMR only revealed the presence of [Pt(H)(AgCl)$_2$(AuPPh$_3$)$_8$]$^+$. This quantitative exchange of NO_3 by Cl gives further evidence for the composition of this cluster being [Pt(H)(AgCl)$_2$(AuPPh$_3$)$_8$]$^+$.

Table 1. Crystal Data for **1**, **2a**, and **2b**

	1	**2a**	**2b**
chem formula	$PtAu_8AgP_8C_{144}H_{121}N_2O_6$	$PtAu_8Ag_2P_8C_{144}H_{121}N_3O_9$	
fw	4102.0	4271.9	4271.9
a/Å	15.475(7)	16.956(3)	16.848(4)
b/Å	26.048(2)	17.48(1)	17.51(4)
c/Å	16.586(2)	27.36(2)	27.40(3)
α/deg	90	93.68(8)	96.3(2)
β/deg	97.00(4)	97.55(4)	95.9(1)
γ/deg	90	76.16(8)	72.46(7)
V/Å^3	6636	7802	7639
Z	2	2	2
space group	$P2_1$ (No.4)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T/°C	20	20	20
λ/Å	0.7107	0.7107	0.7107
estimated solvent ether molecules/cell	3–5	8–9	5–8
ϱ/g cm^{-3}	2.188	1.953	1.966
μ(Mo Kα)/cm$^{-1\,a}$	81.59	87.5	89.4
R^b [I>2σ(I)]	0.070	0.055	0.090
wR$_2{}^c$ [I>2σ(I)]	0.170	0.151	0.230

^{a} Calculated with estimated number of solvent molecules. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

[Pt(H)(AuPPh$_3$)$_8$](NO$_3$) (3). A 100-mg (0.025-mmol) sample of [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$ was dissolved in 5 mL of pyridine under Schlenk conditions. Dihydrogen was bubbled through this solution for 10 min upon which the color changed from brown to dark red. After stirring for 1 h under dihydrogen atmosphere the cluster [Pt(H)(AuPPh$_3$)$_8$](NO$_3$) was precipitated as a red powder by adding H_2-saturated diethyl ether. The red precipitate was filtered under Schlenk conditions and washed with diethyl ether with subsequent drying in vacuum (yield: 80 mg, 0.020 mmol; 80%, calculated for Pt).

IR (solid): in addition to the characteristic bands originating from the PPh_3 ligands only a band from uncoordinated NO_3 (1378 cm^{-1}, broad) could be observed. ^{31}P NMR (CH_2Cl_2, Schlenk): $\delta = 52.1$ ppm with ^2J(P–^{195}Pt) (doublet) = 452 Hz. ^{1}H NMR (hydride): $\delta = +5.4$ ppm with ^3J(H–^{31}P) (nonet) = 14.3; ^1J(H–^{195}Pt) could not be observed due to the low S/N ratio of the hydride signal. ^{195}Pt NMR: $\delta = -5673$ ppm with ^1J(Pt–^{1}H) (doublet) = 721 Hz and ^2J(Pt–^{31}P) (nonet) = 452 Hz. All these data are in perfect agreement with the full characterization given in ref 24.

Structure Determination of 1 and Two Phases of 2

Collection and Reduction of Crystallographic Data. Since single crystals of **1** and **2** decompose very quickly upon removal from the solvent, crystals were mounted in a capillary with a drop of solvent (a mixture of diethyl ether and methanol). X-ray reflection data were measured on an Enraf-Nonius CAD4 diffractometer. Standard experimental details are given elsewhere.[25] Emperical absorption corrections based on a Ψ scan were performed on **1** (see supplementary material) but not for **2** . Single-crystals of **1** appeared to be of reasonable good quality, although, as will be seen later, disorder and unknown solvent molecules caused quite some problems. Crystal data for **1** are given in Table 1. A total of 12 419 reflections were measured (h, 0 to 18; k, 0 to 30; l, −19 to +19); the drift curve showed no decomposition.

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Only very few crystals of **2** were available, and the only one which gave acceptable reflection intensities was used for data collection. Crystal data for **2** are given in Table 1. The crystal was not very good as can be seen from the inaccuracies in the cell dimensions (Table 1, column **2a**). On average, reflection prophiles have a full-width half-maximum of 0.25°; the scan width applied was 1.5°. During measurements on the crystal of **2** a phase transition took place after measurement of about 4900 reflections (during 39 h). The transition was indicated by a slow but continuous diminution of the intensities of the three monitoring reflections. The orientation matrix needed optimization several times allowing the measurement of another 1794 reflections (in about 16 h). The drift curve for the initial 4900 reflections increased from 1.00 to 1.04, and for the additional 1794 reflections from 1.04 to 1.14. The 6694 reflections comprised a very incomplete dataset (h, 0 to 4; k, −17 to +18; l, −28 to 28), $\sin(\theta/\lambda)_{\max} = 0.527$. This first crystalline phase of **2** is denoted **2a**.

Visual inspection of the crystal showed no serious damage. On trying to redetermine the orientation matrix, we found that the unit cell had changed significantly, and consequently the structure is at least slightly different. This phase of **2** is denoted **2b**. As expected, the crystal of **2b** was of poor quality (worse than that of **2a**): the peak shapes of the reflections were about 1.8 times as broad as the corresponding peak shapes of **2a**, and the cell dimensions were inaccurate. Nevertheless, because the dataset of **2a** was very incomplete, and no other crystal was available, we also measured the reflection data of **2b**. This resulted in 7881 reflections; the drift curve increased from 1.00 to 1.06 (h, 0 to 13; k, −12 to +13; l, −21 to +21), $\sin(\theta/\lambda)_{\max} = 0.389$. The two data sets were used to solve the two corresponding (very similar) structures.

Solution and Refinement of the Structure of 1. The structure was partially solved in space group $P2_1/m$. The positions of the metal atoms were found from an automatic orientation and translation search (ORIENT,[26] TRACOR[27]) with a $PtAu_8$ fragment of the cluster compound $[Pt(CO)(AgNO_3)(AuPPh_3)_8](NO_3)_2$[6] as a search model, followed by a phase refinement procedure to expand the fragment (DIRDIF[28]). The phenyl rings were found by searching for the best fit when rotating an idealized phenyl ring around the appropriate axes (Au−P and P−C with Au−P−C = 109°) in the Fourier map. At this stage the phenyl groups appeared to be disordered, due to the presence of mirror plane through the molecule. It was possible to unravel the overlapping phenyl rings to obtain an asymmetric molecule which could be refined properly, in space group $P2_1$. Nevertheless, due to the disorder in the solvent area (see below) some of the phenyl rings showed rather large vibrational amplitudes. One nitrate ion was found coordinating to the silver atom. Another nitrate, and the proton on the platinum atom, which were indicated by the spectroscopic study and the analytical composition, were not found. Of the unknown amount of solvent molecules none could be detected.

The structure was refined by full-matrix least-squares on F_o^2 values using SHELXL[29] with anisotropic parameters for the metal atoms. The phenyl rings and the coordinated nitrate were refined with constrained idealized geometry, and the hydrogen atoms on the phenyl rings were placed on calculated positions (C−H = 0.93 Å). After refinement to an R value of 0.14, an additional empirical absorption correction based on $F_o - |F_c|$ was applied using DIFABS[30] on the original unmerged F_o values. The corrected data were merged ($R_{\text{merge}} = 0.047$, for the $0kl$ reflections) and the structure refined to $R = 0.084$. To improve the refinement of the structure of the cluster, we used the BYPASS method,[31,32] which allows the refinement of the ordered part of a structure in the presence of disordered solvent molecules. The procedure produces reflection data from which the contribution of the disordered solvent area has been subtracted, and these data are used in SHELXL[29] to refine the ordered part of the structure. After the BYPASS procedure and subsequent least-squares refinement with restraints on the Au−P and P−C distances and C−P−C angles, convergence was reached at $R = 0.070$. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2)+(0.074F_c^2)^2]$. A maximum residual density of 1.8 e/Å^3 was found near the metal atoms.

Table 2. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**[a]

	x	y	z	U_{eq}
Pt(1)	2318(1)	2488(1)	2652(1)	24(1)
Au(1)	1208(1)	2484(2)	1303(1)	33(1)
Au(2)	2597(1)	2480(2)	4254(1)	62(1)
Au(3)	3058(2)	1630(1)	3315(2)	43(1)
Au(4)	1338(2)	1659(1)	2495(2)	59(1)
Au(5)	2925(3)	1885(1)	1572(2)	60(1)
Au(6)	2937(2)	3073(1)	1558(2)	48(1)
Au(7)	3075(2)	3336(1)	3316(2)	44(1)
Au(8)	1308(2)	3312(1)	2484(2)	49(1)
Ag(1)	4077(2)	2526(3)	2867(2)	60(1)
P(1)	127(4)	2557(4)	229(3)	28(2)
P(2)	2466(5)	2547(4)	5612(4)	36(2)
P(3)	3715(10)	969(5)	4035(8)	75(6)
P(4)	255(7)	1074(4)	2423(6)	53(3)
P(5)	3812(6)	1430(3)	815(5)	34(2)
P(6)	3327(6)	3660(3)	557(5)	37(2)
P(7)	3877(7)	4015(3)	3956(5)	28(3)
P(8)	173(7)	3848(4)	2876(6)	57(3)
N(1)	5929(21)	2376(17)	3073(18)	197(14)
O(11)	5517(29)	2420(29)	2385(25)	197(14)
O(12)	6741(28)	2339(23)	3148(26)	197(14)
O(13)	5541(29)	2393(26)	3690(24)	197(14)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The BYPASS procedure calculated the volume of the solvent area as 820 Å^3 (12.6 vol %). The electron count of the solvent area was 279 electrons per cell. From the density of liquid diethyl ether the volume of one disordered solvent molecule is estimated to be 170 Å^3. The volume of one NO_3 anion is of the same order of magnitude. If we assume all the solvent molecules in the crystal to be diethyl ether, their number can be calculated from the volume of the solvent area as obtained from the BYPASS procedure. Under the same assumption their number can be calculated from the total number of electrons in the solvent area as obtained by the same procedure. Thus the volume of the solvent area accounts for two uncoordinated NO_3 anions, as demanded by the elemental analysis of the cluster compound, and roughly three ether molecules per unit cell; the electron count of the solvent area agrees with two NO_3 anions and five ether molecules.

Positional and thermal parameters of selected atoms are given in Table 2, and selected bond distances and angles are given in Table 3. The molecular structure of **1** is given in Figure 1A.[33]

Solution and Refinement of the Structure of 2a. The positions of the metal atoms were found from automatic Patterson interpretation (PATTY[34]) followed by a phase refinement procedure to expand the fragment (DIRDIF[28]). The phenyl rings were found by searching for the best fit when rotating an idealized phenyl ring around the appropriate axes (Au−P and P−C with Au−P−C = 109°) in the Fourier map. Two nitrate ions were found, each coordinated to a silver atom. Another nitrate ion and the hydride on the platinum atom, which were indicated by the spectroscopic study and the analytical composition, were not found. Of the unknown amount of solvent molecules none could be detected.

The structure was refined by full-matrix least-squares on F_o^2 values using SHELXL[29] with anisotropic parameters for the metal atoms. The

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Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**, **2a**, and **2b**

		Compound **1**			
Pt(1)–Au(1)	2.650(2)	Au(1)–Au(8)	2.905(4)	Au(7)–Ag(1)	2.773(7)
Pt(1)–Au(2)	2.639(2)	Au(2)–Au(3)	2.846(5)	Au(1)–P(1)	2.299(6)
Pt(1)–Au(3)	2.684(4)	Au(2)–Au(7)	2.867(5)	Au(2)–P(2)	2.293(6)
Pt(1)–Au(4)	2.632(4)	Au(3)–Au(4)	2.839(4)	Au(3)–P(3)	2.265(12)
Pt(1)–Au(5)	2.640(3)	Au(3)–Au(5)	2.948(4)	Au(4)–P(4)	2.258(10)
Pt(1)–Au(6)	2.639(4)	Au(4)–Au(5)	3.105(6)	Au(5)–P(5)	2.298(9)
Pt(1)–Au(7)	2.673(4)	Au(5)–Au(6)	3.095(2)	Au(6)–P(6)	2.387(9)
Pt(1)–Au(8)	2.650(4)	Au(6)–Au(7)	2.977(4)	Au(7)–P(7)	2.341(9)
Pt(1)–Ag(1)	2.703(3)	Au(7)–Au(8)	2.910(4)	Au(8)–P(8)	2.395(11)
Au(1)–Au(4)	2.910(4)	Au(3)–Ag(1)	2.961(8)	Ag(1)–O(11)	2.47(5)
Au(1)–Au(5)	3.066(4)	Au(5)–Ag(1)	3.106(6)	Ag(1)–O(13)	2.52(4)
Au(1)–Au(6)	3.069(4)	Au(6)–Ag(1)	2.986(6)		
Au(1)–Pt(1)–Au(4)	66.85(11)	Au(4)–Pt(1)–Au(5)	72.2(2)	Au(7)–Pt(1)–Ag(1)	62.1(2)
Au(1)–Pt(1)–Au(5)	70.94(10)	Au(5)–Pt(1)–Au(6)	71.80(5)	Pt(1)–Au(1)–P(1)	171.8(2)
Au(1)–Pt(1)–Au(6)	70.84(10)	Au(6)–Pt(1)–Au(7)	68.17(11)	Pt(1)–Au(2)–P(2)	164.8(2)
Au(1)–Pt(1)–Au(8)	66.47(10)	Au(6)–Pt(1)–Au(8)	73.64(14)	Pt(1)–Au(3)–P(3)	172.1(4)
Au(2)–Pt(1)–Au(3)	64.65(13)	Au(7)–Pt(1)–Au(8)	66.27(13)	Pt(1)–Au(4)–P(4)	166.9(4)
Au(2)–Pt(1)–Au(4)	96.6(2)	Au(2)–Pt(1)–Ag(1)	80.15(9)	Pt(1)–Au(5)–P(5)	164.3(3)
Au(2)–Pt(1)–Au(7)	65.31(13)	Au(3)–Pt(1)–Ag(1)	66.7(2)	Pt(1)–Au(6)–P(6)	172.7(3)
Au(2)–Pt(1)–Au(8)	97.76(14)	Au(5)–Pt(1)–Ag(1)	71.1(2)	Pt(1)–Au(7)–P(7)	173.2(3)
Au(3)–Pt(1)–Au(4)	64.56(13)	Au(6)–Pt(1)–Ag(1)	68.0(2)	Pt(1)–Au(8)–P(8)	152.4(3)
Au(3)–Pt(1)–Au(5)	67.25(11)				
		Compound **2a**			
Pt(1)–Au(1)	2.644(5)	Au(2)–Au(7)	2.919(3)	Au(7)–Ag(1)	2.784(7)
Pt(1)–Au(2)	2.647(4)	Au(2)–Au(4)	3.005(5)	Au(7)–Au(8)	2.910(5)
Pt(1)–Au(3)	2.697(5)	Au(2)–Ag(1)	3.037(4)	Au(1)–P(1)	2.319(11)
Pt(1)–Au(4)	2.698(2)	Au(3)–Ag(1)	2.838(4)	Au(2)–P(2)	2.286(8)
Pt(1)–Au(5)	2.671(4)	Au(3)–Ag(2)	2.847(7)	Au(3)–P(3)	2.351(12)
Pt(1)–Au(6)	2.686(3)	Au(3)–Au(5)	2.932(4)	Au(4)–P(4)	2.287(7)
Pt(1)–Au(7)	2.704(3)	Au(3)–Au(4)	3.154(5)	Au(5)–P(5)	2.287(8)
Pt(1)–Au(8)	2.722(5)	Au(4)–Ag(2)	2.805(4)	Au(6)–P(6)	2.304(7)
Pt(1)–Ag(1)	2.784(7)	Au(5)–Ag(2)	2.830(4)	Au(7)–P(7)	2.290(7)
Pt(1)–Ag(2)	2.885(4)	Au(5)–Au(6)	2.846(4)	Au(8)–P(8)	2.338(11)
Au(1)–Ag(2)	2.785(7)	Au(5)–Ag(1)	2.998(6)	Ag(1)–O(12)	2.33(3)
Au(1)–Au(6)	2.909(4)	Au(6)–Au(7)	2.963(4)	Ag(1)–O(11)	2.70(4)
Au(1)–Au(8)	2.934(3)	Au(6)–Au(8)	3.002(4)	Ag(2)–O(21)	2.54(3)
Au(1)–Au(5)	3.155(5)	Au(6)–Ag(1)	3.390(8)	Ag(2)–O(22)	2.54(3)
Au(2)–Au(3)	2.913(3)				
Au(1)–Pt(1)–Au(5)	72.81(12)	Au(6)–Pt(1)–Au(8)	67.43(12)	Au(3)–Pt(1)–Ag(2)	61.2(2)
Au(1)–Pt(1)–Au(6)	66.16(12)	Au(4)–Pt(1)–Au(8)	97.73(13)	Au(4)–Pt(1)–Ag(2)	60.20(9)
Au(5)–Pt(1)–Au(6)	64.18(10)	Au(7)–Pt(1)–Au(8)	64.87(12)	Pt(1)–Au(1)–P(1)	165.2(2)
Au(2)–Pt(1)–Au(3)	66.05(11)	Au(2)–Pt(1)–Ag(1)	67.93(14)	Pt(1)–Au(2)–P(2)	166.1(3)
Au(5)–Pt(1)–Au(3)	66.24(12)	Au(5)–Pt(1)–Ag(1)	66.65(13)	Pt(1)–Au(3)–P(3)	172.8(2)
Au(1)–Pt(1)–Au(4)	92.66(12)	Au(6)–Pt(1)–Ag(1)	76.56(14)	Pt(1)–Au(4)–P(4)	172.9(3)
Au(2)–Pt(1)–Au(4)	68.41(11)	Au(3)–Pt(1)–Ag(1)	62.34(14)	Pt(1)–Au(5)–P(5)	178.5(2)
Au(3)–Pt(1)–Au(4)	71.56(12)	Au(7)–Pt(1)–Ag(1)	60.95(14)	Pt(1)–Au(6)–P(6)	175.6(3)
Au(2)–Pt(1)–Au(7)	66.10(9)	Au(1)–Pt(1)–Ag(2)	60.3(2)	Pt(1)–Au(7)–P(7)	172.3(3)
Au(6)–Pt(1)–Au(7)	66.70(9)	Au(5)–Pt(1)–Ag(2)	61.11(10)	Pt(1)–Au(8)–P(8)	163.3(2)
Au(1)–Pt(1)–Au(8)	66.25(12)				
		Compound **2b**			
Pt(1)-Au(1)	2.650(4)	Au(2)–Au(7)	2.958(7)	Au(7)–Ag(1)	2.802(6)
Pt(1)–Au(2)	2.651(5)	Au(2)–Au(4)	3.022(7)	Au(7)–Au(8)	2.942(5)
Pt(1)–Au(3)	2.725(4)	Au(2)–Ag(1)	3.037(9)	Au(1)–P(1)	2.273(12)
Pt(1)–Au(4)	2.708(8)	Au(3)–Ag(2)	2.860(7)	Au(2)–P(2)	2.273(12)
Pt(1)–Au(5)	2.667(6)	Au(3)–Ag(1)	2.901(9)	Au(3)–P(3)	2.338(12)
Pt(1)–Au(6)	2.698(7)	Au(3)–Au(5)	2.955(7)	Au(4)–P(4)	2.266(14)
Pt(1)–Au(7)	2.740(7)	Au(3)–Au(4)	3.106(6)	Au(5)–P(5)	2.314(12)
Pt(1)–Au(8)	2.729(4)	Au(4)-Ag(2)	2.792(8)	Au(6)–P(6)	2.301(12)
Pt(1)–Ag(1)	2.810(7)	Au(5)–Ag(2)	2.836(9)	Au(7)–P(7)	2.263(12)
Pt(1)–Ag(2)	2.906(8)	Au(5)–Au(6)	2.874(5)	Au(8)–P(8)	2.325(12)
Au(1)–Ag(2)	2.826(7)	Au(5)–Ag(1)	3.005(7)	Ag(1)–O(12)	2.29(5)
Au(1)–Au(6)	2.913(7)	Au(6)–Au(7)	2.931(6)	Ag(1)–O(11)	2.72(4)
Au(1)–Au(8)	2.964(5)	Au(6)–Au(8)	3.071(7)	Ag(2)–O(22)	2.18(10)
Au(1)–Au(5)	3.138(5)	Au(6)–Ag(1)	3.370(6)	Ag(2)–O(21)	2.56(8)
Au(2)–Au(3)	2.904(5)				
Au(1)–Pt(1)–Au(5)	72.32(14)	Au(2)–Pt(1)–Au(7)	66.5(2)	Au(4)–Pt(1)–Ag(2)	59.5(2)
Au(1)–Pt(1)–Au(6)	66.0(2)	Au(6)–Pt(1)–Au(7)	65.2(2)	Au(3)–Pt(1)–Ag(2)	61.0(2)
Au(5)–Pt(1)–Au(6)	64.8(2)	Au(8)–Pt(1)–Au(7)	65.10(13)	Pt(1)–Au(1)–P(1)	164.2(3)
Au(1)–Pt(1)–Au(4)	94.2(2)	Au(2)–Pt(1)–Ag(1)	67.5(2)	Pt(1)–Au(2)–P(2)	165.1(3)
Au(2)–Pt(1)–Au(4)	68.7(2)	Au(5)–Pt(1)–Ag(1)	66.5(2)	Pt(1)–Au(3)–P(3)	174.0(2)
Au(2)–Pt(1)–Au(3)	65.38(12)	Au(6)–Pt(1)–Ag(1)	75.4(2)	Pt(1)–Au(4)–P(4)	173.6(3)
Au(5)–Pt(1)–Au(3)	66.4(2)	Au(3)–Pt(1)–Ag(1)	63.2(2)	Pt(1)–Au(5)–P(5)	179.4(3)
Au(4)–Pt(1)–Au(3)	69.7(2)	Au(7)–Pt(1)–Ag(1)	60.6(2)	Pt(1)–Au(6)–P(6)	175.3(2)
Au(1)–Pt(1)–Au(8)	66.85(12)	Au(1)–Pt(1)–Ag(2)	60.9(2)	Pt(1)–Au(7)–P(7)	172.8(2)
Au(6)–Pt(1)–Au(8)	68.9(2)	Au(5)–Pt(1)–Ag(2)	61.0(2)	Pt(1)–Au(8)–P(8)	164.0(3)
Au(4)–Pt(1)–Au(8)	97.7(2)				

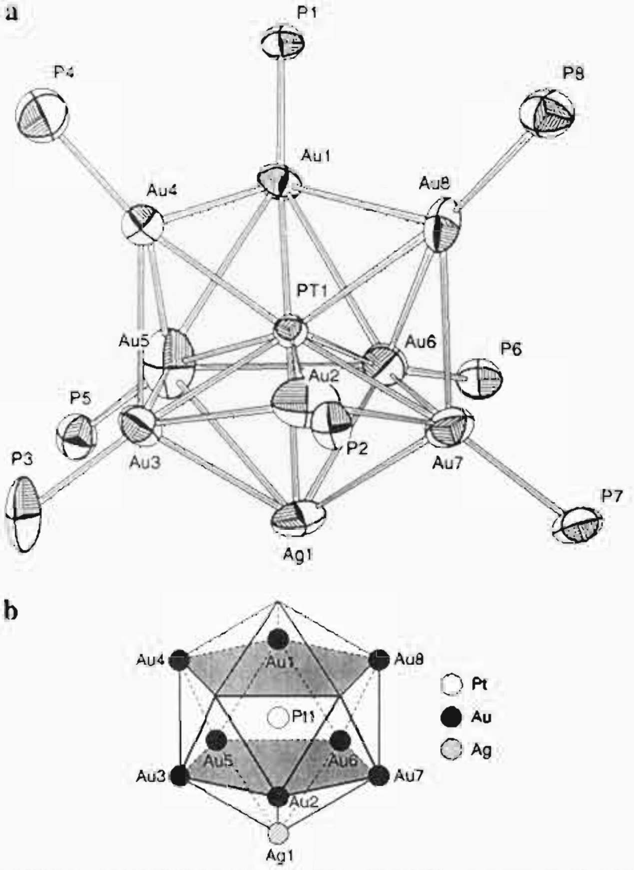

Figure 1. (A) X-ray structure of **1** with atom labeling for Au, Ag, Pt, and P. Phenyl rings and NO_3 groups have been omitted for the sake of clarity. Thermal ellipsoids are at 50% probability. (B) Schematic representation of the metal core of **1**.

phenyl rings and the coordinated nitrate groups ions were refined with constrained idealized geometry, and the hydrogen atoms on the phenyl rings were placed at calculated positions (C−H = 0.93 Å). After refinement to an R value of 0.14, an empirical absorption correction based on $F_o - |F_c|$ was applied using DIFABS[30] on the original unmerged F_o values. The corrected data were merged ($R_{merge} = 0.043$) and the structure refined to $R = 0.080$. To further refine the structure of the cluster we used the BYPASS method.[31,32] After two cycles of the BYPASS procedure and subsequent least-squares refinement with SHELXL[29] with restraints on the Au−P and P−C distances refining to a common value with estimated standard deviations for Au−P = 0.02 Å, C−P = 0.01 Å, and C−C = 0.02 Å and C−P−C angles, convergence was reached at $R = 0.055$. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2)+(0.075F_c^2)^2]$. A maximum residual density of 0.99 e/Å^3 was found near the metal atoms.

The BYPASS procedure calculated the volume of the solvent area as 1912 Å^3 (24.5 vol %). This volume accounts for two uncoordinated NO_3 anions, as demanded by the elemental analysis, and for ca. nine ether molecules per unit cell. The electron count of the solvent area was 389 electrons per cell, which represents two NO_3 anions and roughly eight ether molecules.

Positional and thermal parameters of selected atoms are given in Table 4, and selected bond distances and angles are given in Table 3. The molecular structure of **2a** is given in Figure 4A.[33]

Solution and Refinement of the Structure of 2b. As the unit cell dimensions of **2a** and **2b** differ only slightly and the crystal kept its shape after the transition, it was assumed that the structures did not differ much. Thus to solve the structure the positions of the metal atoms of **2b** were taken from **2a**, followed by a phase refinement procedure to locate the phosphorous atoms and some light atoms (DIRDIF[28]). The phenyl rings and two nitrate ions were found as in the structure determination of **2a**. The third nitrate ion and the proton on the platinum atom were not found. Of the unknown amount of solvent molecules none could be detected.

Table 4. Selected Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2a**[a]

	x	y	z	U_{eq}
Pt(1)	6980(2)	7349(1)	7534(1)	32(3)
Au(1)	8266(2)	7497(1)	8160(1)	48(3)
Au(2)	6091(2)	6701(1)	6833(1)	38(3)
Au(3)	5771(2)	6833(1)	7859(1)	45(3)
Au(4)	7416(2)	5761(1)	7545(1)	70(3)
Au(5)	6417(2)	8147(1)	8331(1)	43(3)
Au(6)	7170(2)	8833(1)	7657(1)	35(3)
Au(7)	6548(2)	8174(1)	6699(1)	38(3)
Au(8)	8250(2)	7570(1)	7090(1)	50(3)
Ag(1)	5390(4)	8261(1)	7347(1)	65(6)
Ag(2)	7307(4)	6569(1)	8462(1)	59(5)
P(1)	9523(6)	7293(4)	8644(2)	62(3)
P(2)	5619(5)	6040(4)	6151(2)	44(2)
P(3)	4611(7)	6539(4)	8117(2)	58(3)
P(4)	7939(5)	4432(4)	7601(2)	50(3)
P(5)	5954(5)	8854(4)	9011(2)	49(3)
P(6)	7227(5)	10137(4)	7771(2)	37(2)
P(7)	6003(5)	8880(3)	6008(2)	40(2)
P(8)	9335(6)	7391(4)	6615(2)	58(3)
N(1)	3669(17)	9016(9)	7176(4)	76(12)
O(11)	3798(23)	8302(9)	7063(7)	70(8)
O(12)	4252(17)	9320(12)	7324(8)	77(9)
O(13)	2959(16)	9426(16)	7141(10)	129(14)
N(2)	7711(18)	5577(10)	9317(6)	73(10)
O(21)	7235(26)	6236(15)	9341(10)	135(13)
O(22)	8086(25)	5380(16)	8951(11)	143(14)
O(23)	7812(31)	5116(14)	9658(9)	135(14)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The structure was refined analogously to **2a**. After refinement to an R-value of 0.14 a DIFABS[30] correction was applied. The corrected data were merged ($R_{merge} = 0.057$) and the structure refined to $R = 0.11$. To improve the refinement of the structure of the cluster we used the BYPASS method.[31,32] After two cycles of the BYPASS procedure and subsequent least-squares refinement with SHELXL,[29] with restraints on the Au−P and P−C distances refining to a common value with estimated standard deviations for Au−P = 0.02 Å, C−P = 0.01 Å, and C−C = 0.02 Å and C−P−C angles, convergence was reached at $R = 0.090$. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2)+(0.067F_c^2)^2]$. A maximum residual density of 3.91 e/Å^3 was found near the metal atoms.

The BYPASS procedure calculated the volume of the solvent area as 1642 Å^3 (21.5 vol %). This volume accounts for two uncoordinated NO_3 anions and roughly eight ether molecules. The electron count of the solvent area was 255 electrons per cell, which represents two NO_3 anions and roughly five ether molecules.

Positional and thermal parameters of selected atoms are given in Table 5, and selected bond distances and angles are given in Table 3.

Note about the similarity of **2a** and **2b**: the unit cell volumes of **2a** and **2b** differ slightly due to the loss of solvent molecules when the transition took place. Projection of the two clusters on top of each other showed that a few phenyl rings have small differences in orientations. As the differences of the metal−phosphorus skeletons are insignificant, we will refer to the structures **2a** and **2b** as structure **2** in the discussion of the molecular structures. Therefore the molecular structure of **2b** is not shown separately.

Results and Discussion

Synthesis, Characterization and Crystal Structure of $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (1). **1** is obtained from the reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $AgNO_3$ in methanol under dihydrogen atmosphere. Because we know that the addition of H_2 is a very fast reaction as compared to the addition of Ag^+, we think that after oxidative addition to give $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$,[12] one of the H-ligands is replaced by electrophilic substitution of $AgNO_3$. **1** can also be obtained from the reaction of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ in alkaline methanol; this reaction probably proceeds through nucleophilic

Table 5. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2b**[a]

	x	y	z	U_{eq}
Pt(1)	7121(2)	7251(2)	7461(1)	31(1)
Au(1)	8401(2)	7407(2)	8070(1)	45(1)
Au(2)	6231(2)	6618(2)	6769(1)	46(1)
Au(3)	5899(2)	6769(2)	7800(1)	39(1)
Au(4)	7581(2)	5629(2)	7452(1)	59(1)
Au(5)	6509(2)	8104(2)	8278(1)	43(1)
Au(6)	7251(2)	8759(2)	7590(1)	39(1)
Au(7)	6669(2)	8093(2)	6640(1)	42(1)
Au(8)	8421(2)	7370(2)	6988(1)	47(1)
Ag(1)	5474(3)	8244(3)	7312(2)	54(2)
Ag(2)	7458(3)	6482(3)	8378(2)	57(2)
P(1)	9621(7)	7167(5)	8550(3)	60(6)
P(2)	5791(5)	5951(5)	6086(4)	49(6)
P(3)	4761(7)	6494(5)	8084(3)	60(6)
P(4)	8113(6)	4279(7)	7469(3)	76(7)
P(5)	5981(5)	8854(6)	8984(4)	42(6)
P(6)	7249(5)	10081(6)	7714(3)	31(5)
P(7)	6129(6)	8792(6)	5975(4)	44(6)
P(8)	9545(6)	7106(5)	6505(4)	60(6)
N(1)	3699(19)	9008(18)	7208(9)	126(28)
O(11)	3855(23)	8276(18)	7090(15)	68(15)
O(12)	4278(24)	9302(25)	7347(19)	115(21)
O(13)	2966(21)	9446(22)	7188(18)	107(19)
N(2)	7788(28)	5645(33)	9195(19)	159(33)
O(21)	7301(44)	6327(36)	9277(29)	225(39)
O(22)	8009(60)	5407(56)	8773(23)	321(60)
O(23)	8056(53)	5201(45)	9536(28)	262(47)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

attack of the methanolate ion to the platinum atom and subsequent β-H transfer to give **1** and formaldehyde, in analogy with published methods to prepare other hydride containing mixed-metal−gold clusters.[24] The reaction of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ with dihydrogen in dichloromethane (or methanol) is the third method of synthesis that gives **1** in high yield. **1** was characterized by elemental analysis, ICP analysis, conductometry in methanol, and IR, ^{1}H NMR, ^{31}P NMR and ^{195}Pt NMR spectroscopy. The solid-state structure of this cluster compound was determined by means of a single-crystal X-ray analysis.

NMR Spectroscopy. ^{31}P, ^{195}Pt and ^{1}H NMR data are given in Table 6. The ^{31}P NMR spectrum of **1** (CH_2Cl_2) consists of one signal at $\delta = 54.7$ ppm due to the fluxional behaviour of the phosphine sites of this cluster; this phenomenon is commonly observed for this type of cluster compounds.[35] The magnitude of the J(P−^{195}Pt) is in the range normally found for a ^2J coupling through a gold nucleus,[6,8,36] this shows that the platinum atom is in the center-position of this cluster surrounded by $AuPPh_3$ units. The doublet structure of the ^{31}P NMR signal, arising from the ^3J(P−Ag), clearly shows the presence of one silver atom. The magnitude of this ^3J(P−Ag) is in the range normally observed for this type of clusters.[6] Because the difference between the separate ^{107}Ag and ^{109}Ag couplings is covered by the line width of the ^{31}P NMR signal (approximately 10 Hz) only the averaged ^3J(P−Ag) is observed.

The separate doublet structure originating from ^{109}Ag and ^{107}Ag is clearly visible in the ^{195}Pt{^{1}H,^{31}P} NMR spectrum (Figure 2A) and proves the presence of one Ag atom directly bonded to the central platinum atom. The ratio of ^1J(Pt−^{109}Ag)/^1J(Pt−^{107}Ag) = 1.15 is in perfect agreement with the value of 1.15 dictated by the ratio of gyromagnetic constants of these two silver isotopes. The magnitude of these ^1J(Pt−Ag) couplings is in the range normally observed.[6]

The ^{195}Pt{^{31}P} NMR spectrum (Figure 2B) clearly shows the presence of a doublet splitting due to ^1J(Pt−H) = 716 Hz; this pattern shows the presence of one hydride ligand directly attached to the platinum. The magnitude of this ^1J(Pt−H) is in the range normally found for hydride containing PtAu cluster compounds,[2,24] but is much smaller than observed for terminal Pt−H, e.g. in *trans*-$Pt(H)(Cl)(PEt_3)_2$ where ^1J(Pt−H) = 1276 Hz.[38] It is therefore believed that in **1** as well as in the aforementioned hydride containing PtAu clusters the hydride ligand is bridging between platinum and peripheral metal (gold) atoms.

The presence of eight $AuPPh_3$ units bonded to the platinum atom in **1** gives rise to a nonet caused by ^2J(Pt−^{31}P), but because the ^1J(Pt−Ag) couplings give rise to a doublet structure and are in the same range as this ^2J(Pt−^{31}P), the overall ^{195}Pt{^{1}H} NMR spectrum (Figure 2C, supplementary material) results in an even multiplet that can be perfectly simulated (Figure 2D, supplementary material). The hydride signal in the ^{1}H NMR spectrum of **1** is observed at $\delta = +1.74$ ppm, this tremendous low-field shift, as compared to those for mononuclear terminal platinum hydrides,[38] is an additional indication toward a bridging position of the hydride ligand in **1**. It is known that hydride chemical shifts are observed significantly low-field in Pt/Au− and other M/Au−hydride-bridged systems.[15,16,39−41]

Crystal Structure. The X-ray structure analysis of the solid shows that the cluster framework consists of 10 metal atoms (Figure 1A): the platinum atom is situated in the center position (as seen from the NMR experiments) and surrounded by eight gold atoms and one silver atom; each of the gold atoms is bonded to a triphenylphosphine group, and a nitrate group is coordinated to the silver atom. The metal framework of **1** matches that of the isoelectronic cluster $[Pt(CO)(AgNO_3)(AuPPh_3)_8](NO_3)_2$ very closely.[6] The silver atom is positioned at the bottom-vertex of an icosahedron and the eight gold atoms are placed at eight adjacent vertices (Figure 1B); the platinum atom is situated in the center. Icosahedral based geometries are often observed for mixed-metal−gold cluster compounds with an $(S^\sigma)^2(P^\sigma)^6$ electron configuration (18 electrons).[6,21,42]

Although the hydride ligand could not be located in the X-ray analysis directly, the area where this hydride is to be found is clear from the metal positions: the three unoccupied vertices of the icosahedron (Figure 1B) define a region that is most likely occupied by the hydride ligand in a bridging position as concluded from spectral considerations. This implies that the hydride ligand is bridging between platinum and gold atoms.

It is noteworthy that the silver atom, which is less electronegative than gold, is positioned in the metal-triangle "trans" to the fictitious triangle where the relatively electronegative H-ligand is to be found. The preference of H to bridge between Pt and Au over Pt and Ag is interesting; both possiblities are well documented.[15]

The Pt−Au distances (2.632−2.684 Å) and the Au−Ag distances (2.773−3.106 Å) are in the range normally found in

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Table 6. ^{195}Pt NMR Data for **1**, **2**, and **3**[a,b]

	^{31}P	^{195}Pt	^{1}H
$[Pt(H)(AuPPh_3)_8](NO_3)$	$\delta = 52.1$ $^2J(^{31}P-^{195}Pt)(d) = 452$	$\delta = -5673$ $^1J(^{195}Pt-^1H)$ (d) $= 721$ $^2J(^{195}Pt-^{31}P)$ (n) $= 452$	$\delta = 5.4$ $^3J(^1H-^{31}P)$ (n) $= 14.3$ $^1J(^1H-^{195}Pt)$ not obsd
$[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$	$\delta = 54.7$ $^2J(^{31}P-^{195}Pt)$ (d) $= 412$ $^3J(^{31}P-Ag)$ (d) $= 19$	$\delta = -6036$ $^1J(^{195}Pt-^1H)$ (d) $= 716$ $^1J(^{195}Pt-^{109}Ag)$ (d) $= 487$ $^1J(^{195}Pt-^{107}Ag)$ (d) $= 425$ $^2J(^{195}Pt-^{31}P)$ (n) $= 412$	$\delta = 1.74$ $^1J(^1H-Ag)$ (d) $= 19.7$ $^3J(^1H-^{31}P)$ (n) $= 12.5$ $^1J(^1H-^{195}Pt)$ not obsd
$[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$	$\delta = 54.0$ $^2J(^{31}P-^{195}Pt)$ (d) $= 411$ $^3J(^{31}P-Pt)$ (d) $= 17$		
$[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$	$\delta = 58.6$ $^2J(^{31}P-^{195}Pt)$ (d) $= 407$ $^3J(^{31}P-Ag)$ (t) $= 19$	$\delta = -6347.6$ $^1J(^{195}Pt-^1H)$ (d) $= 611$ $^1J(^{195}Pt-^{109}Ag)$ (t) $= 465$ $^1J(^{195}Pt-^{107}Ag)$ (t) $= 405$ $^2J(^{195}Pt-^{31}P)$ (n) $= 407$	
$[Pt(H)(AgCl)_2(AuPPh_3)_8](NO_3)$	$\delta = 57.6$ $^2J(^{31}P-^{195}Pt)$ (d) $= 406$ $^3J(^{31}P-Ag)$ (t) $= 16$		

[a] Chemical shifts are given in ppm; coupling constants are given in Hz. [b] Key: d = doublet, t = triplet, and n = nonet.

$(S^\sigma)^2(P^\sigma)^6$ PtAuAg clusters.[11] The Au(2)−Ag(1) distance (3.440 Å) is much longer. The Pt−Ag distance (2.703 Å) is short as compared to Pt−Ag distances in compounds known from the literature[5,6,42,43,44] (range 2.75−2.79 Å).

In the crystalline state one of the nitrates is coordinated to the silver, whereas no other nitrates were found within coordinating distances from any metal atom. This is also observed in the solid IR spectrum where bands at 1292 and 1351 cm^{-1} were present, originating from coordinated NO_3 and uncoordinated NO_3 respectively. The solution IR only reveals the presence of uncoordinated NO_3 groups, which suggests **1** in solution to be $[Pt(H)(Ag)(AuPPh_3)_8]^{2+}$, where the peripheral Ag may be solvated by methanol. The dissociation of the NO_3 group from the silver in solution is also concluded from the large conductivity of **1** in a methanol solution: the $\Lambda_m{}^0$ of 224 S·cm^2·mol^{-1} of **1** indicates it to be a 2:1 electrolyte.

Acidimetric Titration. The reaction of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ with dihydrogen in methanol yields **1** in quantitative amounts. **1** can be precipitated from this methanol solution with water. Subsequent filtration and acidimetric titration of the methanol−water filtrate reveals the presence of one H$^+$ per used Pt in agreement with eq 1 (cluster **1** remained intact during this treatment).

$$[Pt(Ag)(AuPPh_3)_8]^{3+} + H_2 \rightarrow [Pt(H)(Ag)(AuPPh_3)_8]^{2+} + H^+ \quad (1)$$

This reaction shows that the Brønsted acidity of the hypothetical intermediate dihydride $[Pt(H)_2(Ag)(AuPPh_3)_8]^{3+}$ is considerably larger than that of the related known dihydride $[Pt(H)_2(AuPPh_3)_8]^{2+}$. A relatively strong base like pyridine is needed to abstract a proton from this dihydride, resulting in the corresponding monohydride $[Pt(H)(AuPPh_3)_8]^+$ (**3**) (vide infra). The presence of an addition Lewis acid (Ag$^+$) on the $PtAgAu_8$ cluster as compared to the $PtAu_8$ cluster may be the main reason for its enhanced Brønsted acidity.

Synthesis and Characterization of $[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$. The compound $[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$ was prepared in good yield (78%) from the reaction of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ in alkaline methanol and subsequent treatment with dichloromethane and addition of $\{(n\text{-Bu})_4N\}PF_6$. This cluster was characterized by ICP analysis and ^{31}P NMR spectroscopy; the synthesis is largely equal to route B used to synthesize **1** (see Experimental Section). The dichloromethane used under these alkaline conditions obviously provides the chloride to make the Ag−Cl bond. The IR spectrum of this cluster shows a band at 258 cm^{-1} and the absence of both coordinated and uncoordinated NO_3. We assign the band at 258 cm^{-1} to the Ag−Cl stretching vibration as a band at 257 cm^{-1} was found for $Pt(H)(AgCl)_2(AuPPh_3)_8NO_3$ for which the presence of two Ag−Cl bonds is clearly demonstrated. The CH_2Cl_2 used in the synthesis must then be the origin of the Cl. However the precence of AgOH instead of AgCl cannot be excluded, the band at 258 cm^{-1} could be due to Ag−OH stretching vibration. Elemental analyses up till now were not conclusive . The synthesis of $Pt(H)(AgCl)(AuPPh_3)_8{}^+$ from **1** and LiCl was not successful. The characterization shows that the compound, be it either $Pt(H)(AgOH)(AuPPh_3)_8PF_6$ or $[Pt(H)(AgCl)(AuPPh_3)_8](PF_6)$ must be closely related to **1**.

Synthesis, Characterization and Crystal Structure of $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (2). $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**2**) can be prepared by reacting $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (**1**) with $AgNO_3$ in methanol. In this reaction the metal core of **1** is extended with one silver atom by means of electrophilic addition. **2** can also be obtained from the reaction of $[Pt(H)(AuPPh_3)_8](NO_3)$ (**3**) with $AgNO_3$ in a molar ratio of 1:2; in this reaction the nine-metal-atom cluster **3** is extended with two silver atoms through electrophilic addition of $AgNO_3$. However, the preferred method of synthesis for **2** is the quantitative reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $AgNO_3$ (molar ratio 1:2) under dihydrogen atmosphere.

NMR Spectroscopy. ^{31}P, ^{195}Pt NMR data are given in Table 6. The ^{31}P NMR spectrum of **2** (CH_2Cl_2) consists of one signal at $\delta = 58.6$ ppm as a result of the fluxional behaviour of the phosphine sites in solution at ambient temperatures. The magnitude of $J(P-{}^{195}Pt)$ shows it to be a ^2J coupling. The NMR appearance thus clearly indicated that **2** has one platinum atom, which is in the central position surrounded by $AuPPh_3$ units.

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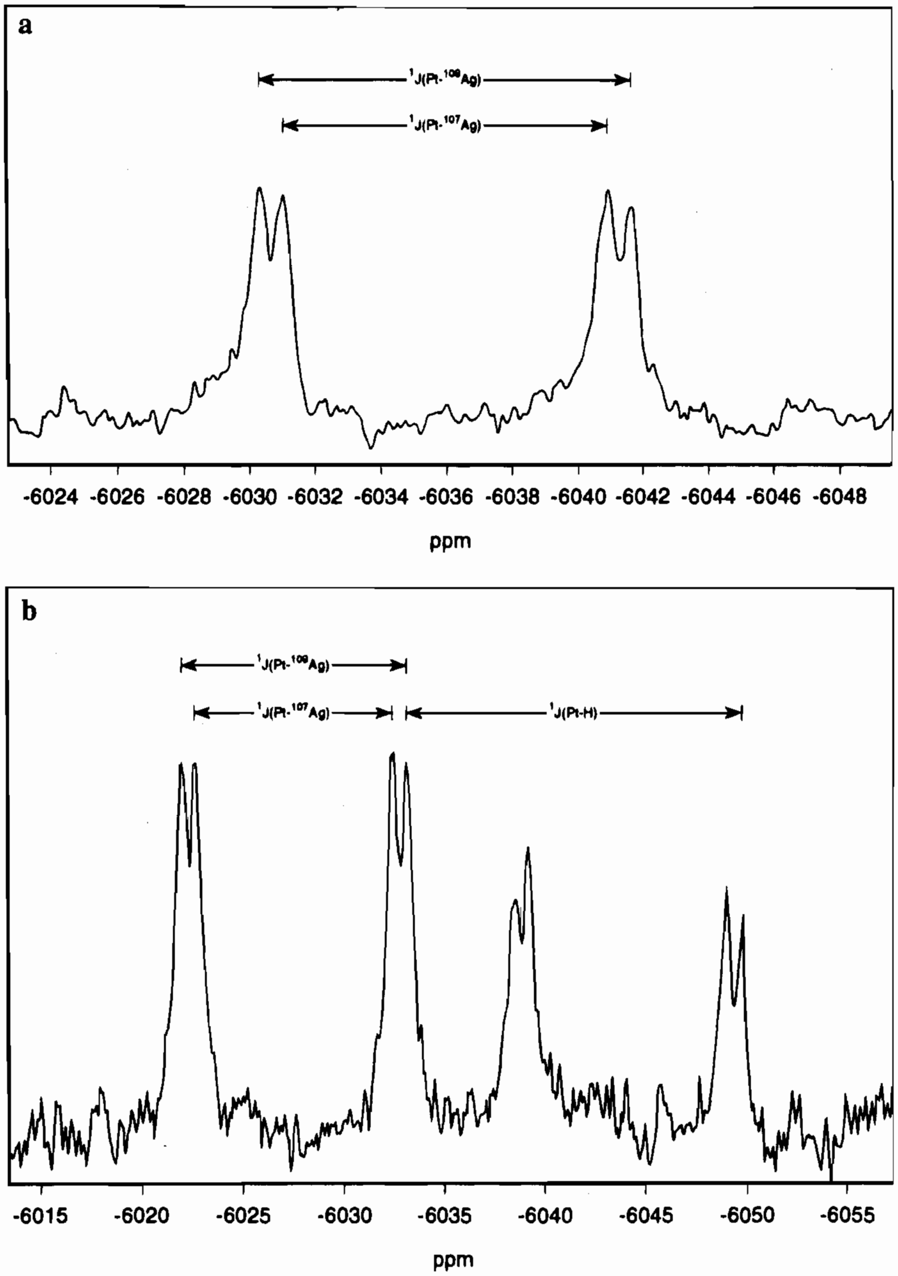

Figure 2. (A) ^{195}Pt{^{1}H,^{31}P} NMR spectrum and (B) ^{195}Pt{^{31}P} NMR spectrum of [Pt(H)(AgNO$_3$)(AuPPh$_3$)$_8$](NO$_3$) (**1**) (43.02 MHz).

The triplet structure of the ^{31}P NMR signal, arising from the ^3J(P–Ag), clearly shows the presence of two silver atoms in the periphery of **2**. The triplet structure originating from the two silver atoms is clearly visible in the ^{195}Pt{^{1}H,^{31}P} NMR spectrum (Figure 4A). Separate ^{107}Ag and ^{109}Ag couplings were obtained from the complex ^{195}Pt NMR spectra without ^{31}P-decoupling. The presence of one hydride ligand in **2** was clearly shown from the ^{195}Pt{^{31}P} NMR spectrum where a doublet splitting due to ^1J(Pt–H) = 611 Hz is present (Figure 4B). The magnitude of this ^1J(Pt–H) is comparable to that of **1** and therefore it is concluded that the hydride in **2** is also bridging between platinum and peripheral metal (gold) atoms.

The presence of eight AuPPh$_3$ units in **2** is clear from elemental analysis and ICP results. In addition to this the ^{195}Pt NMR spectra without ^{31}P-decoupling also show the presence of eight such AuPPh$_3$ units, two silver atoms and one hydride ligand, resulting in a complex splitting pattern that can be matched perfectly by simulation using the reported coupling constants.

When we compare the scalar coupling constants between Pt and H, Ag or P for compounds [Pt(H)(AuPPh$_3$)$_8$](NO$_3$) (**3**), [Pt(H)(AgNO$_3$)(AuPPh$_3$)$_8$](NO$_3$) (**1**) and [Pt(H)(AgNO$_3$)$_2$(AuPPh$_3$)$_8$](NO$_3$) (**2**) we see that these constants decrease in the order **3** > **1** > **2** (see Table 6). All of the three compounds are (S$^\sigma$)^2(P$^\sigma$)^6 clusters but in going from **3** to **1** and from **1** to **2** one additional Pt–Ag bond has to be formed. So the bond orders between the central platinum, the hydride, the silver atoms, and the gold atoms decrease in going from cluster **3** to **1** and finally to **2**. This must be related to the afore-mentioned decrease in ^1J(Pt–H), ^1J(Pt–Ag), and ^2J(Pt–^{31}P) respectively. This decrease in bond orders is also in agreement with the observed increase in (mean) Pt–Au and Pt–Ag bond lengths when going from **1** to **2** (vide infra).

Crystal Structure. The solid-state structure of cluster **2** is known from two X-ray determinations (see Structure Determination) (Figure 3A). It shows that the metal core consists of 11 metal atoms: the central position is occupied by the platinum atom (as seen from NMR experiments) and is surrounded by eight gold atoms and two silver atoms. The gold atoms are

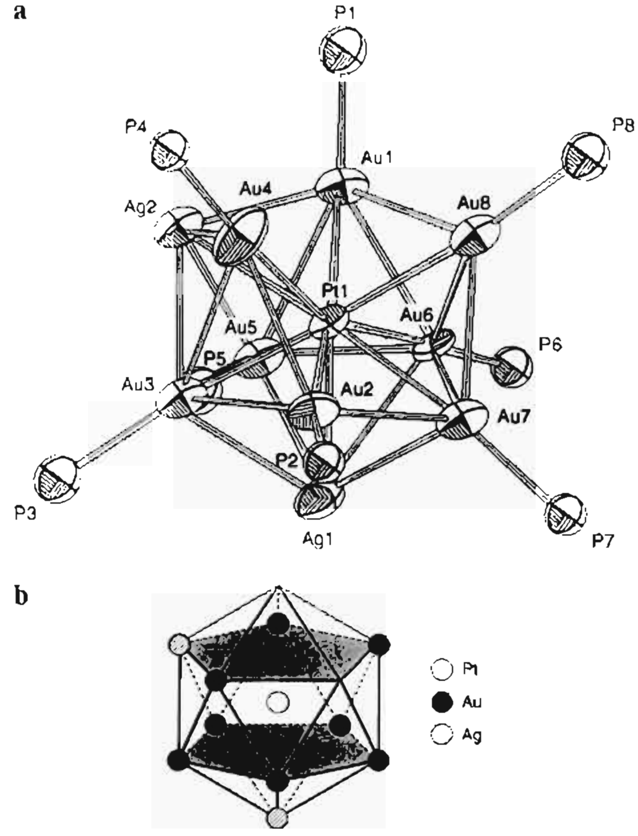

Figure 3. (A) X-ray structure of **2a** (first phase of **2**) with atom labeling for Au, Ag, Pt, and P. Phenyl rings and NO_3 groups have been omitted for the sake of clarity. Thermal ellipsoids are at 50% probability. (B) Schematic representation of the metal core of **2**.

bonded to triphenylphosphine ligands, whereas both silver atoms are bonded to nitrate groups. The metal framework of **2**, like that of **1**, is based on an icosahedral geometry as shown in Figure 3B. Cluster **2**, as compared to **1**, has one more vertex occupied, which results in a more spherical surrounding of the central platinum atom, the silver atoms (Ag(1) and Ag(2)) are occupying positions with high connectivities, and the positions with lowest connectivity are occupied by gold atoms Au(4) and Au(8).

The two adjacent unoccupied vertices of the icosahedron (Figure 3B) define the region that is most likely occupied by the bridging hydride ligand. This implies that the hydride ligand is positioned "trans" to Ag(1) (Figure 3A); Ag(2) is remarkably pushed out of the partially filled five-membered ring Au(8)−Au(1)−Ag(2)−Au(4), away from the aforementioned hydride region.

The Pt−Au distances range from 2.644 to 2.722 Å in **2a** and from 2.650 to 2.740 Å in **2b**. The mean Pt−Au distance in both modifications of **2** is longer than in **1**. The Pt−Ag distances, 2.784 and 2.885 Å in **2a** and 2.810 and 2.906 Å in **2b**, are definitely longer than in **1** and are normal, compared to Pt−Ag distances observed in other platinum−silver compounds.[6,15,42−44] These longer radial Pt to metal distances are in agreement with the lowering in bond order of Pt−Au and Pt−Ag bonds in going from **1** to **2** as already discussed with regard to the scalar coupling constants in the ^{195}Pt NMR spectra of these cluster compounds.

The conductivity of **2** in methanol solution ($\Lambda_m{}^O$ = 195 S·cm^2·mol^{-1}) is indicative of a 2:1 electrolyte and shows that in solution a partial dissociation of the two silver-bonded NO_3 groups has occurred, indicating **2** in solution to be $[Pt(H)(Ag)(AgNO_3)(AuPPh_3)_8]^{2+}$, where one of the peripheral Ag atoms is probably solvated by methanol. In the solid state, however, both silver atoms are coordinated to nitrate groups. These observations are also clear from the IR spectra. The solid IR spectrum shows the presence of uncoordinated NO_3 (1346 cm^{-1}) and of coordinated NO_3 (1286 cm^{-1}); in the solution IR spectrum of **2** the band originating from coordinated NO_3 (1295 cm^{-1}) is also present but its relative intensity is roughly halved with respect to that in the IR spectrum of the solid sample. It may be related to the high positive charge of the hypothetical cluster $[Pt(H)(Ag)_2(AuPPh_3)_8]^{3+}$ that full dissociation of both silver-bonded NO_3 groups of **2** in solution does not occur. The absence of a terminal Pt−H stretching vibration in the IR spectra of **2** supports the proposed bridging position of the hydride ligand.

Acidimetric Titration. The reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $AgNO_3$ in a molar ratio of 1:2 under dihydrogen atmosphere in methanol quantitatively yields the cluster compound **2**. If **2** is precipitated from this methanol solution with water and subsequently filtered off (**2** remained intact during this treatment), the methanol−water filtrate can be shown to contain one H$^+$ per used Pt by means of acidimetric titration. This is seen from the net reaction given in eq 2.

$$[Pt(AuPPh_3)_8]^{2+} + 2AgNO_3 + H_2 \rightarrow [Pt(H)(Ag)(AgNO_3)(AuPPh_3)_8]^{2+} + NO_3^- + H^+ \quad (2)$$

Synthesis and Characterization of $[Pt(H)(AgCl)_2(AuPPh_3)_8](NO_3)$. The reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $[Ag(PPh_3)Cl]_4$ (molar Pt:Ag ratio = 1:2) under dihydrogen atmosphere in dichloromethane results in $[Pt(H)(AgCl)_2(AuPPh_3)_8](NO_3)$ in 68% yield. The presence of two silver atoms was clear from ICP results and from the triplet structure of the ^{31}P NMR signal due to ^3J(P−Ag). The ICP analysis also showed the presence of eight gold atoms and eight phosphines. The IR spectrum clearly revealed the presence of uncoordinated NO_3 (1349 cm^{-1}); the Ag−Cl stretching vibration (257 cm^{-1}) was also observed in the IR spectrum. The conductivity in methanol ($\Lambda_m{}^O$ = 93 S·cm^2·mol^{-1}) showed that this cluster is a 1:1 electrolyte. The formulation of this cluster in solution therefore is given by $[Pt(H)(AgCl)_2(AuPPh_3)_8]^+$.

Quantitative exchange of the nitrates in **2** by Cl using LiCl also results in $[Pt(H)(AgCl)_2(AuPPh_3)_8]^+$. This reaction provides further evidence for this cluster to be the AgCl-analogue of **2**.

Synthesis and Characterization of $[Pt(H)(AuPPh_3)_8](NO_3)$ (3). The reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with dihydrogen is known to yield $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$.[12] However, when this reaction is performed in a strong basic solvent like pyridine the monohydride $[Pt(H)(AuPPh_3)_8](NO_3)$ (**3**) is formed in good yield (Figure 5). It was shown to be identical to the compound obtained from the reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with alkaline methanol.[24] The compound is sensitive to protonation by water to yield the dihydride cluster which releases H_2 very easily, thereby giving the starting compound $[Pt(AuPPh_3)_8](NO_3)_2$. Compound **3** should therefore be handled under standard Schlenk conditions.

The presence of only one signal in the ^{31}P NMR spectrum of **3** shows that this cluster also has fluxional phosphine sites in solution. The magnitude of J(P−^{195}Pt) = 452 Hz clearly shows this to be a ^2J coupling. This implies that the platinum atom is in central position surrounded by $AuPPh_3$ units as in the parent compound $[Pt(AuPPh_3)_8](NO_3)_2$ and as in **1** and **2**.

The ^{195}Pt NMR resonance is observed at $\delta = -5673$ ppm. The ^1J(Pt−H) = 721 Hz which is in the range observed for **1** and **2** and other known hydride containing PtAu cluster

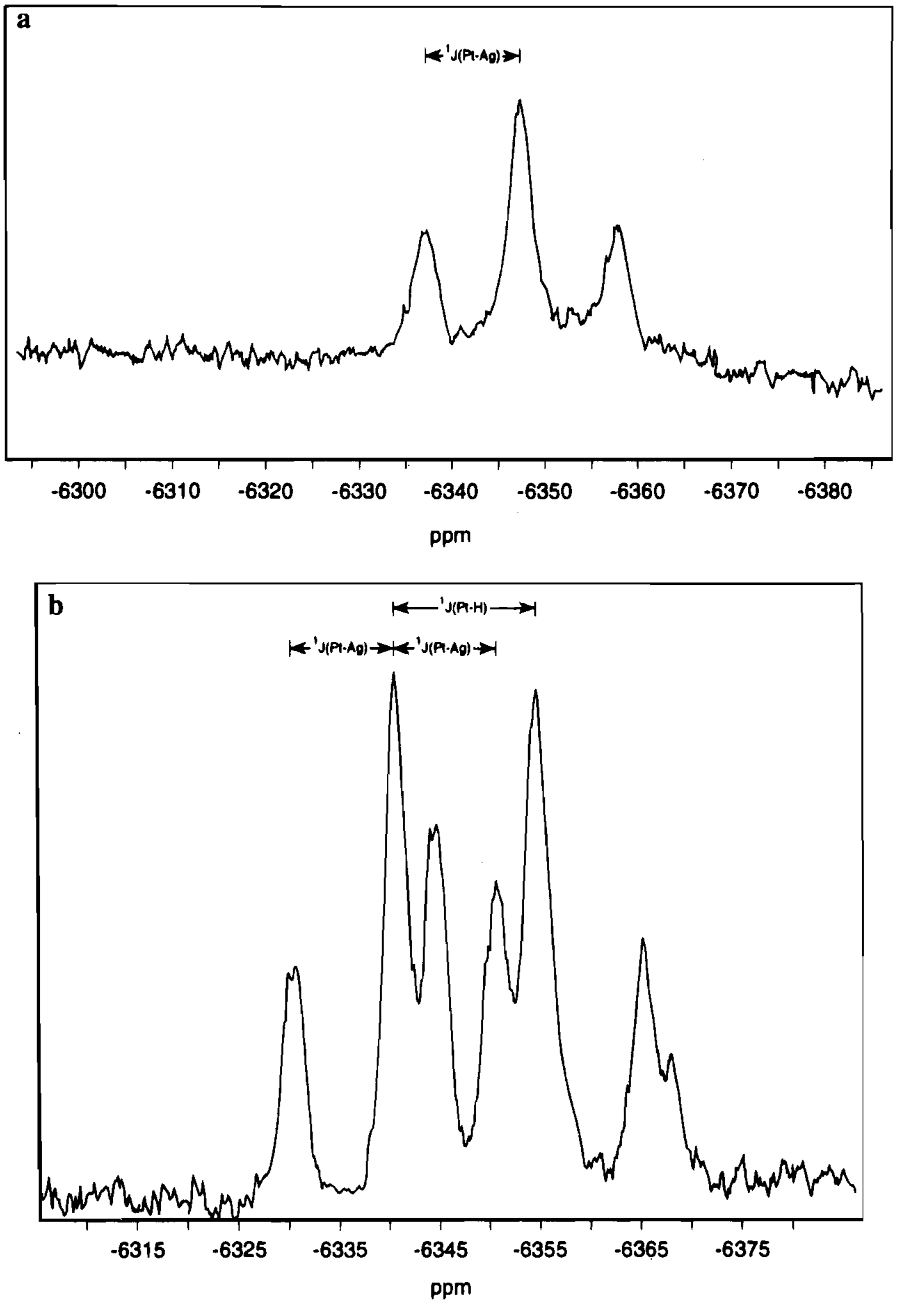

Figure 4. (A) $^{195}Pt\{^1H,^{31}P\}$ NMR spectrum and (B) $^{195}Pt\{^{31}P\}$ NMR spectrum of $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**2**) (43.02 MHz).

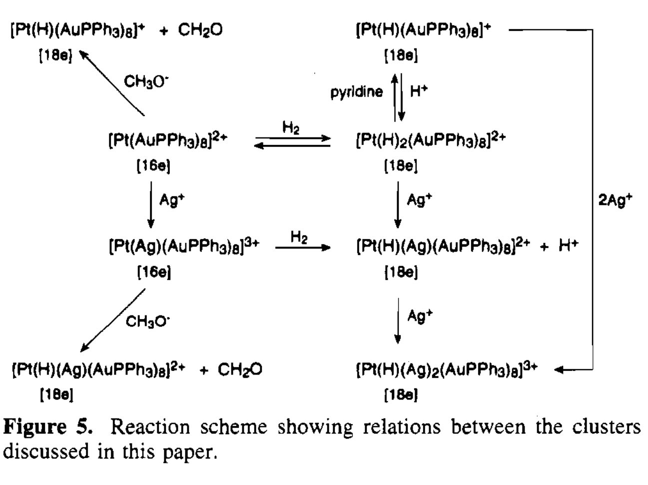

Figure 5. Reaction scheme showing relations between the clusters discussed in this paper.

compounds.[2,12,24] This shows that the hydride ligand is bridging between the central platinum atom and peripheral gold atoms like proposed for **1** and **2**. Additional support for this is found from the ^1H NMR hydride chemical shift at +5.4 ppm, and the absence of a terminal Pt–H stretching vibration in the IR spectrum of **3**.

In this paper we have seen some intimate details of how the reaction of silver(I) compounds with H_2 precipitates metal: a nine-metal-atom particle ($[Pt(AuPPh_3)_8](NO_3)_2$) grows via oxidative addition of H_2, deprotonation, and electrophilic addition of Ag^+ to a 10- and then to an 11-metal-atom particle, $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$. The electron count has a pronounced effect on the habitus of the metal embryo, and the attachment of hydrogen and silver atoms occurs on locally separated sites. It is well-established that silver does not precipitate on pure silver or gold when using H_2 as reducing agent for Ag^+, although this reaction is thermodynamically favorable. This is due to the large overpotential for this reduction with H_2 on pure silver or gold metal. The spontaneous growth of metal clusters by precipitation of silver as seen in this paper, on the other hand, provocatively suggests that the overpotential for this reduction of silver(I) by H_2 has dropped to a considerable extent, due to the presence of a Pt atom to which H_2 adds oxidatively.

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Supplementary Material Available: Tables of crystallographic details and additional fractional positional parameters, anisotropic thermal parameters, and bond distances and angles and Figure 2C,D, showing overall and simulated $^{195}Pt\{^1H\}$ NMR spectra for **1** (39 pages). Ordering information is given on any current masthead page.

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