Halide derivatives of palladium–gold cluster compounds. X-ray crystal and molecular structure of $(I)Pd(AuPPh_3)_7(AuI)_2$

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Abstract

The reaction chemistry of $[Pd(AuPPh_3)_8](NO_3)_2$ with the halide ions Cl^-, Br^- and I^- and with the pseudohalide CN^- has been studied. Acetone solutions of $[Pd(AuPPh_3)_8](NO_3)_2$ reacted with these ions to give the new Pd–Au clusters $(I)Pd(AuPPh_3)_7(AuI)_2$, $[Pd(AuPPh_3)_7(AuBr)_3]^+$, $Pd(AuPPh_3)_8(AuCl)_3$ and $Pd(AuPPh_3)_8(AuCN)_3$, respectively. In the presence of added acid the reaction with Cl^- yielded the cationic cluster $[Pd(AuPPh_3)_7(AuCl)_3]^+$. The structure of $(I)Pd(AuPPh_3)_7(AuI)_2$ has been determined by X-ray diffraction (unit cell: $P2_1/n$, $a=37.29$, $b=22.69$, $c=16.639$ Å, $\beta=114.61°$, $Z=4$, $V=12\,800$ Å^3, refinement: $R=0.069$). The geometry of this cluster is that of a Pd-centered icosahedral fragment in accord with its eighteen-electron configuration. The coordinated iodine anion of this cluster can be displaced by reaction with CO to give $[(CO)Pd(AuPPh_3)_7(AuI)_2]^+$, while the sixteen-electron clusters $[Pd(AuPPh_3)_7(AuBr)_3]^+$ and $[Pd(AuPPh_3)_7(AuCl)_3]^+$ reacted cleanly with CO to give simple adducts. The eighteen-electron clusters $Pd(AuPPh_3)_8(AuCl)_3$ and $Pd(AuPPh_3)_8(AuCN)_3$ showed no reaction with CO. The mechanism of these interesting cluster fragmentation and growth reactions is discussed.

Introduction

The study of phosphine stabilized, mixed metal–gold clusters has resulted in the preparation of a large number of new compounds which have shown interesting structural and reactivity properties [1–5]. Some of the Pt–Au clusters reversibly react with H_2 and show surprising catalytic activity as molecular solids for H_2–D_2 equilibration ($H_2+D_2 \rightarrow 2HD$) and for the oxidation of H_2 and CO [6]. The turnover frequency for the catalytic H_2–D_2 equilibration with solid $[Pt(AuPPh_3)_8](NO_3)_2$ is similar to that of an activated platinum surface. In this context, such clusters should be excellent models for H_2 and O_2 activation on bimetallic M–Au surfaces [7, 8].

Recent studies with Pt–Au cluster compounds illustrate the usefulness of electron counting rules in rationalizing structure and reactivity [1–5, 9, 10]. For example, the sixteen-electron cluster $[Pt(AuPPh_3)_8]^{2+}$ has a flattened, toroidal geometry and reacts with two-electron donors to give eighteen-electron clusters with spheroidal geometry. An example is the reaction with CO to give the stable cluster $[(CO)Pt(AuPPh_3)_8]^{2+}$ [10]. Another is the reaction of the sixteen-electron cluster $[(PPh_3)Pt(AuPPh_3)_6]^{2+}$ with halide ions (X = Br and I) to give simple eighteen-electron adducts $[(X)(PPh_3)Pt(AuPPh_3)_6]^+$ [9]. The reaction of $[Pt(AuPPh_3)_8]^{2+}$ with halides (X = Cl and I) has also been studied but in this case a more complicated cluster fragmentation and growth reaction occurs [4].

$$[Pt(AuPPh_3)_8]^{2+} + X^- \longrightarrow (PPh_3)Pt(AuPPh_3)_6(AuX)_3$$

The $PtAu_9$ product is an eighteen-electron cluster with a spheroidal geometry best described as that of a Pt centered, icosahedral fragment.

The chemistry of the palladium analogues such as $[Pd(AuPPh_3)_8]^{2+}$ and $[(PPh_3)Pd(AuPPh_3)_6]^{2+}$ is much less developed compared with that of the Pt–Au clusters, and although some of the chemistry is similar, there are important differences [5, 11]. For example, $[Pd(AuPPh_3)_8]^{2+}$ reacts *reversibly* with CO and shows no reaction with H_2. It is also a much less active catalyst for H_2–D_2 equilibration compared with its Pt analogue [12]. In this paper we report the reaction chemistry of $[Pd(AuPPh_3)_8]^{2+}$ with halide ions and with the cyanide ion. A series of new $PdAu_{9,10,11}$ clusters result. The

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products are very different from those isolated from similar reactions with $Pt(AuPPh_3)_8]^{2+}$. This study is important as it extends our knowledge of the reactivity of mixed metal–gold cluster compounds and will help in the design of new syntheses and catalytic studies.

Experimental

Physical methods and reagents

^{31}P and ^{13}C NMR spectra were recorded at 121.421 and 75.5 MHz, respectively, with the use of a Varian VXR-300 MHz spectrometer. Both were run with proton decoupling, and ^{31}P NMR spectra are reported in ppm relative to the internal standard trimethyl phosphate (TMP), with positive shifts downfield. Conductivity measurements were made with the use of a Yellow Springs model 35 conductance meter. Compound concentrations used in the conductivity experiments were 3×10^{-4} M in CH_3CN unless otherwise noted. FAB-MS experiments were carried out with the use of a VG Analytical, Ltd., 7070E-HF high-resolution double-focusing mass spectrometer equipped with a VG 11/250 data system [13, 14]. All FAB-MS experiments were done with use of a *m*-nitrobenzyl alcohol, MNBA, matrix. IR spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer. Microanalyses were carried out by Analytische Laboratorien, Engelskirchen, Germany. Solvents were dried and distilled prior to use. $[Pd(AuPPh_3)_8](NO_3)_2$ was prepared as described in the literature [5]. PPNCl ($[Ph_2P{=}N{=}PPh_2][Cl]$) was prepared and purified as described in the literature [14]. Benzoic acid, $[Bu_4N][I]$, $[Et_4N][Br]$, $NaBH_4$, KCN and NH_4PF_6 were used without further purification. All manipulations were carried out under a purified N_2 atmosphere with use of standard inert atmosphere techniques unless otherwise noted.

Preparation of compounds

$(I)Pd(AuPPh_3)_7(AuI)_2$ (1)

This was prepared by combining with stirring a 10 ml acetone solution of $[Pd(AuPPh_3)_8](NO_3)_2$ (300 mg, 7.68×10^{-2} mmol) with a 5 ml acetone solution of $[Bu_4N][I]$ (68 mg, 1.84×10^{-1} mmol). Within 5 min a dark purple, microcrystalline product precipitated from a dark red solution. The solid was collected on a sintered-glass frit and washed with acetone and diethyl ether. Recrystallization by vapor diffusion of diethyl ether into an acetone solution gave dark purple crystals of **1**. Yield 220 mg (88%, based on I). **1** is soluble in dichloromethane and chloroform and slightly soluble in acetone; insoluble in alcohols, saturated hydrocarbons, and diethyl ether. ^{31}P NMR (CH_2Cl_2, r.t.): δ 45 (v br s). FAB-MS: *m/z* 4095 ($M = (I)Pd(AuPPh_3)_7(AuI)_2$), 3968 ($M-I$), 3706 ($M-I-PPh_3$), 3444 ($M-I-2PPh_3$). *Anal.* Calc. for **1**, $Au_9PdP_7C_{126}H_{105}I_3$: C, 36.95; H, 2.59; P, 5.29; I, 9.29. Found: C, 37.32; H, 2.59; P, 5.65; I, 10.19%.

$[Pd(AuPPh_3)_7(AuBr)_3](NO_3)$ (2(NO₃))

This was prepared by dissolving $[Pd(AuPPh_3)_8](NO_3)_2$ (100 mg, 2.56×10^{-2} mmol) and $[Et_4N][Br]$ (25 mg, 7.68×10^{-2} mmol) in 3 ml dry acetone and heating at 50 °C under N_2 while stirring for 2 h. The red precipitate which formed was collected on a sintered-glass frit, washed with acetone and diethyl ether, and dried under a stream of N_2. Yield 46 mg (53%, based on Au). **2**(NO_3) is soluble in dichloromethane, insoluble in alcohols, acetone and diethyl ether, and slightly soluble in acetonitrile. **2**(PF_6) was obtained by adding 2 ml of a dichloromethane solution of **2**(NO_3) (35 mg, 7.6×10^{-3} mmol) to 5 ml of a stirred methanol solution of NH_4PF_6 (25 mg, 0.152 mmol). A red precipitate formed after several minutes. The product was collected on a sintered-glass frit, washed with diethyl ether, and dried under a stream of N_2. Yield 30 mg (86%, based on **2**(NO_3)). **2**(PF_6) is soluble in dichloromethane, acetone and nitromethane, slightly soluble in acetonitrile and methanol, and insoluble in diethyl ether. ^{31}P NMR of **2** (CD_2Cl_2, r.t.): δ 46 (v br s), (CD_2Cl_2, −80 °C): δ 52.5 (br s, int = 2), 45 (br s int = 1), 42.5 (br s, int = 4). FT-IR of **2**(PF_6) (KBr): $\nu(PF_6)$ 840 cm^{-1}. FAB-MS of **2**(PF_6): *m/z* 4151 ($Pd(AuPPh_3)_7(AuBr)_3 = M$) 4073 ($M-Br$), 3875 ($M-Au-Br$), 3613 ($M-Au-Br-PPh_3$), 3416 ($M-2Au-Br-PPh_3$), 3336 ($M-2Au-2Br-PPh_3$). The equivalent conductance of **2**(PF_6) (57.8 cm^2 mho mol^{-1}) is indicative of a 1:1 electrolyte in CH_3NO_2. *Anal.* Calc. for **2**(NO_3), $Au_{10}PdP_7C_{126}H_{105}Br_3NO_3$: C, 35.91; H, 2.52; Br, 5.69. Found: C, 36.70; H, 2.78; Br, 5.07%.

$[(CO)Pd(AuPPh_3)_7(AuBr)_3](NO_3)$ (3(NO₃))

This was prepared by stirring 1.5 ml of a dichloromethane solution of **2**(NO_3) (7 mg, 2.4×10^{-3} mmol) under 1 atm of CO for 1 h. The brown precipitate which formed upon the addition of 15 ml of diethyl ether was collected on a sintered-glass frit, washed with diethyl ether and dried with a stream of CO. All solutions of **3**(NO_3) were kept under a CO atm since the CO is labile. The isotopically labeled analog $[(^{13}CO)Pd(AuPPh_3)_7(AuBr)_3](NO_3)$, was prepared by the same procedure with ^{13}CO substituted for CO. ^{31}P NMR (CH_2Cl_2, r.t.): δ 40 (v br s), 45 (v br s). ^{13}C NMR (CD_2Cl_2, r.t.): δ 217.9 (oct, $J(^{13}C{-}P)$ 7.5 Hz). FT-IR (KBr): $\nu(CO)$ 1977 cm^{-1}.

$[Pd(AuPPh_3)_7(AuCl)_3](NO_3)$ (4(NO₃))

This was prepared by adding 15 ml of an acetone solution of $[Pd(AuPPh_3)_8](NO_3)_2$ (112 mg, 2.87×10^{-2} mmol) to a flask charged with PPNCl (49.5 mg, 8.62×10^{-2} mmol) and benzoic acid (17.6 mg, 0.144

mmol). Three drops of distilled water were added to the dark red solution via syringe. The solution was allowed to stir under N_2 for 24 h during which time it lightened to red–orange in color. The solution was filtered and evaporated to dryness under vacuum. The solid residue was redissolved in 10 ml methanol, stirred and filtered through diatomaceous earth on a sintered glass frit. The filtrate was evaporated to dryness. This process was repeated using 5 ml methanol, 10 ml ethanol and 10 ml THF, respectively, to remove impurities. Toluene (10 ml) was added to the final solid residue and an orange–brown precipitate formed. This was collected on a glass frit. Yield 33.9 mg (40%, based on Au). The PF_6^- salt, **4**(PF_6), was obtained by adding a 20-fold excess of NH_4PF_6 to **4**(NO_3) in a minimal amount of methanol. The resulting cluster which precipitated was collected on a sintered-glass frit, rinsed with diethyl ether, and dried under a N_2 stream. **4**(NO_3) was soluble in acetone, alcohols, dichloromethane and THF, insoluble in Et_2O and toluene. ^{31}P NMR (CD_2Cl_2, r.t.): δ 44.6 (v br s). The ^{31}P NMR spectrum became resolved as the temperature was lowered to −80 °C. ^{31}P NMR (CD_2Cl_2, −80 °C): δ 53.1 (J(P–P) = 10 and 27 Hz, int = 2, doublet of triplets), δ 43.7 (J(P–P) = *c.* 29 Hz, int = 1, mult), δ 42.7 (int = 2, br mult), δ 42.3 (J(P–P) = *c.* 10 Hz, int = 2, mult). Equivalent conductance (78.5 cm^2 mho mol^{-1}) was indicative of a 1:1 electrolyte in CH_3CN solution. FAB-MS: *m/z* 4269 (M = {$[Pd(AuPPh_3)_7(AuCl)_3](PF_6)$ + matrix fragment $C_6H_4CH_2O$}), 4007 ($M - PPh_3$), 3862 ($M - PPh_3 - PF_6$), 3600 ($M - 2PPh_3 - PF_6$), 3403 ($M - Au - 2PPh_3 - PF_6$).

*$[(CO)Pd(AuPPh_3)_7(AuCl)_3](NO_3)$ (**5**(NO_3))*

This was prepared by stirring 3 ml of a dichloromethane solution of **4**(NO_3) (40.1 mg, 9.83×10^{-3} mmol) under an atmosphere of CO for 20 min. Diethyl ether (20 ml) was added while maintaining a CO atmosphere. The red precipitate which formed was collected on a sintered-glass frit, washed with diethyl ether and dried under a stream of N_2. Solution samples were kept under a CO atmosphere since the CO was labile. The isolated yield was 60%. The isotopically labeled analog, $[(^{13}CO)Pd(AuPPh_3)_7(AuCl)_3](NO_3)$, was prepared by the same procedure. ^{31}P NMR (CD_2Cl_2, r.t.): δ 44.3 (s). ^{13}C NMR (CD_2Cl_2, r.t.): δ 217.5 (oct, $J(^{13}C–P)$ 4.5 Hz). FT-IR (KBr): ν(CO) 1979 cm^{-1}.

*$Pd(AuPPh_3)_8(AuCl)_3$ (**6**)*

This was prepared by reacting $[Pd(AuPPh_3)_8](NO_3)_2$ (50 mg, 1.3×10^{-2} mmol) with PPNCl (73.5 mg, 1.28×10^{-1} mmol) with use of 8 ml of acetone as solvent. The solution was stirred for 3 h with the formation of an orange precipitate. The reaction can be run for a shorter time at 50 °C with a slightly lower yield. The solid product was collected on a sintered-glass frit and washed with diethyl ether. Yield 6.9 mg (16%, based on Au). The orange solid was soluble in dichloromethane and insoluble in methanol, acetone, diethyl ether, acetonitrile, nitromethane and hexanes. ^{31}P NMR (CH_2Cl_2, r.t.): δ 40.5, 50.7 (s) and δ 48.9 and 42.5 assigned to unreacted $[Pd(AuPPh_3)_8]^{2+}$ and $[Au(PPh_3)_2]^+$, respectively. FAB-MS: *m/z* 4478 ($M = Pd(AuPPh_3)_8(AuCl)_3$), 4244 ($M - Cl - Au$). *Anal.* Calc. for **6**, $Au_{11}PdP_8C_{144}H_{120}Cl_3$: C, 38.62; H, 2.71; P, 5.53; Cl, 2.38. Found: C, 37.78; H, 2.61; P, 5.12; Cl, 2.91%.

*$Pd(AuPPh_3)_8(AuCN)_3$ (**7**)*

This was prepared by the reaction of a 4 ml dichloromethane solution of $[Pd(AuPPh_3)_8](NO_3)_2$ (50 mg, 1.28×10^{-2} mmol) with a 3 ml methanol solution of KCN (4.4 mg, 6.76×10^{-2} mmol). A dark red color formed immediately. Over the course of 3 h of stirring at room temperature a brown precipitate formed. The precipitate was collected on a sintered-glass frit and rinsed with diethyl ether. Yield 45.6 mg (69%, based on Au). Compound **7** was soluble in dichloromethane, acetone (slightly) and nitromethane, insoluble in diethyl ether, alcohols, hexanes and acetonitrile. ^{31}P NMR (CH_2Cl_2, r.t.): δ 44.8 (s). FT-IR (KBr): ν(CN) 2156, 2144 cm^{-1}. FAB-MS: *m/z* 4448 ($M = Pd(AuPPh_3)_8(AuCN)_3$), 4186 ($M - PPh_3$), 3964 ($M - Au - PPh_3 - CN$), 3701 ($M - Au - 2PPh_3 - CN$), 3504 ($M - 2Au - 2PPh_3 - CN$), 3281 ($M - 3Au - 2PPh_3 - 2CN$).

X-ray structure determination

Collection and reduction of X-ray data

A summary of crystal data for **1** is presented in Table 1. The crystal was attached to the end of a glass fiber with use of epoxy resin. The crystal class and space group were unambiguously determined by the Enraf-Nonius CAD4 peak search, centering and indexing programs [15], and by successful solution and refinement of the structure (*vide infra*). The intensities of three standard reflections were measured every 1.5 h of X-ray exposure time during data collection and no decay was noted for either crystal. The data were corrected for Lorentz, polarization and background effects. An empirical absorption correction was applied by use of the program DIFABS [16]. All data were collected using an Enraf-Nonius CAD-4 diffractometer with controlling hardware and software [15], and all calculations were performed using the Molecular Structure Corporation TEXSAN crystallographic software package [17], run on a Microvax 3 computer.

Solution and refinement of the structure

The structure was solved by direct methods [18, 19]. Full-matrix least-squares refinement and difference Fourier calculations were used to locate most of the

TABLE 1 Crystallographic data for $(I)Pd(AuPPh_3)_7(AuI)_2$ (**1**)

Crystal parameters and measurement of intensity data	
Space group	$P2_1/n$ (No 14)
Cell parameter T (°C)	24
a (Å)	37.29(2)
b (Å)	22 69(1)
c (Å)	16.639(4)
β (°)	114 61(3)
V (Å^3)	12800
Z	4
Density (calc.) (g cm^{-3})	2 125
Radiation (Å)	graphite monochromated Mo Kα (0 71073)
Absorption coefficient (cm^{-1})	112.2
Transmission factors: max., min.	1 61, 0.61
Formula	$C_{126}H_{105}I_3P_7Au_9Pd$
Formula weight (amu)	4095 84
Refinement by full-matrix least-squares	
R^a	0.069
$R_w{}^a$	0.085

[a] The function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$, where $\omega=4F_o{}^2/s^2(F_o)^2$. The unweighted and weighted residuals are defined as $R=\Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|$ and $R_w=[(\Sigma\omega(|F_o|-|F_c|)^2)/(\Sigma w|F_o|^2)]^{1/2}$.

remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation [20] and the effects of anomalous dispersion were included in F_c by using the values of Δf and $\Delta f'$ given by Cromer, and Ibers and Hamilton [21]. The metal and iodine atoms were refined with anisotropic thermal parameters. The phenyl carbon atoms were refined as rigid groups with fixed geometry. The orientations and temperature factors of these groups were allowed to refine. This procedure was used because several of the phenyl rings showed signs of disorder which could not be adequately modeled. The use of rigid groups was considered to be a better model under this circumstance. This procedure is often used with large clusters as disorder in the ligands is common and has little effect on the geometry of the metal core. Phenyl hydrogen atoms were included in their idealized positions. The final positional and thermal parameters of the refined atoms within the coordination core are given in Table 2. An ORTEP drawing of the cluster core including the labeling scheme is shown in Fig. 1. Table 3 gives selected distances and angles within the cluster core. See also 'Supplementary material'.

Results

The transformations observed in this study are summarized in Scheme 1. All of the compounds listed were isolated as solids and characterized by spectroscopic and analytical methods. Compound **1** was characterized by single crystal X-ray diffraction. Characterization data and relevant crystallographic results are given in 'Experimental' and Table 1–3 and are discussed in the next section.

TABLE 2 Positional parameters and their e.s d s for core atoms in $(I)Pd(AuPPh_3)_7(AuI)_2$[a]

Atom	x	y	z	B (Å^2)
Au1	0 36812(7)	0.2469(1)	0.0221(2)	2 3(1)
Au2	0 40821(7)	0.30225(9)	0 1934(2)	2 4(1)
Au3	0.40269(7)	0.21857(9)	0 3204(2)	2 1(1)
Au4	0.41529(7)	0 1798(1)	0.1716(2)	2.4(1)
Au5	0 31853(8)	0 2249(1)	0.2818(2)	2.6(1)
Au6	0 34967(7)	0.12385(9)	0.2369(2)	2 4(1)
Au7	0 27515(7)	0.17852(9)	0 1101(2)	2.0(1)
Au8	0.29058(7)	0.2636(1)	0.0032(2)	2.6(1)
Au9	0.32855(7)	0.14225(9)	0 0392(2)	2.3(1)
I	0 3260(1)	0 3427(1)	0 1948(3)	3.7(2)
I1	0.3831(2)	0 2727(2)	−0.1142(4)	7.3(3)
I6	0.3636(1)	0.0191(2)	0.3114(4)	4.7(2)
Pd	0.3468(1)	0.2293(2)	0 1579(3)	1 3(2)
P2	0.4489(5)	0.3799(6)	0 219(1)	3 2(4)
P3	0.4430(5)	0 2216(6)	0 469(1)	3 0(4)
P4	0 4649(5)	0 1252(6)	0 162(1)	3.5(4)
P5	0 2873(5)	0.2382(6)	0 374(1)	3 1(4)
P7	0 2116(5)	0.1419(6)	0.064(1)	2 7(4)
P8	0.2547(5)	0.3334(7)	−0.100(1)	3 7(4)
P9	0.3186(5)	0.0577(6)	−0 045(1)	3 1(4)

[a] For phenyl group positional parameters see 'Supplementary material'. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$

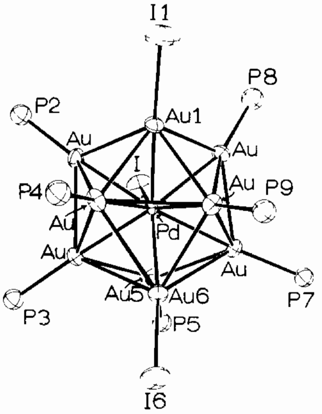

Fig. 1 ORTEP drawing of the coordination core of **1**. Ellipsoids are drawn with 50% probability boundaries and phenyl rings have been omitted for clarity The Au atoms have the same labels as the P or I atoms to which they are attached.

Discussion

Synthesis and spectroscopic characterization of the clusters

$(I)Pd(AuPPh_3)_7(AuI)_2$ (**1**) was prepared by combining $[Pd(AuPPh_3)_8](NO_3)_2$ and $[Bu_4N][I]$ in acetone solution

TABLE 3. Selected bond lengths (Å) and bond angles (°) with e.s.d.s for the cluster core of $(I)Pd(AuPPh_3)_7(AuI)_2$

Bond lengths			
Au1–Au2	2.897(4)	Au6–Pd	2.711(5)
Au1–Au4	2.820(4)	Au7–Au8	2.842(4)
Au1–Au8	2.801(4)	Au7–Au9	2.828(5)
Au1–Au9	2.871(4)	Au7–Pd	2.706(5)
Au1–I1	2.617(8)	Au7–P7	2.32(2)
Au1–Pd	2.720(7)	Au8–Au9	3.040(3)
Au2–Au3	2.911(4)	Au8–Pd0	2.670(5)
Au2–Au4	2.829(3)	Au8–P8	2.31(2)
Au2–Pd	2.686(5)	Au9–Pd0	2.673(5)
Au2–P2	2.25(2)	Au9–P9	2.31(2)
Au3–Au4	2.845(5)	I–Pd	2.829(6)
Au3–Au5	2.932(4)	Au4–Au6	3.316(5)
Au3–Au6	2.859(3)		
Au3–Pd	2.650(5)		
Au3–P3	2.30(2)		
Au4–Au9	3.179(4)		
Au4–Pd	2.712(6)		
Au4–P4	2.29(2)		
Au5–Au6	2.807(4)		
Au5–Au7	2.834(4)		
Au5–I	3.109(5)		
Au5–Pd	2.678(7)		
Au5–P5	2.30(2)		
Au6–Au7	2.971(3)		
Au6–Au9	3.076(4)		
Au6–I6	2.631(5)		
Bond angles			
Au3–Pd–Au8	168.1(2)	Au5–Pd–Au7	63.5(2)
Au3–Pd–Au9	122.4(2)	Au5–Pd–Au6	62.8(1)
Au3–Pd–Au5	66.8(2)	Au5–Pd–Au4	125.3(2)
Au3–Pd–Au2	66.1(1)	Au5–Pd–Au1	171.8(2)
Au3–Pd–Au7	121.4(2)	Au5–Pd–I	68.7(2)
Au3–Pd–Au6	64.4(1)	Au2–Pd–Au7	167.0(2)
Au3–Pd–Au4	64.1(1)	Au2–Pd–Au6	125.4(2)
Au3–Pd–Au1	118.9(2)	Au2–Pd–Au4	63.2(1)
Au3–Pd–I	91.8(2)	Au2–Pd–Au1	64.8(2)
Au8–Pd–Au9	69.4(1)	Au2–Pd–I	71.1(2)
Au8–Pd–Au5	110.5(2)	Au7–Pd–Au6	66.5(1)
Au8–Pd–Au2	106.7(2)	Au7–Pd–Au4	128.9(2)
Au8–Pd–Au7	63.8(1)	Au7–Pd–Au1	114.4(2)
Au8–Pd–Au6	125.6(2)	Au7–Pd–I	97.2(2)
Au8–Pd–Au4	122.4(2)	Au6–Pd–Au4	75.4(1)
Au8–Pd–Au1	62.6(1)	Au6–Pd–Au1	124.5(2)
Au8–Pd–I	76.6(1)	Au6–Pd–I	131.1(3)
Au9–Pd–Au5	118.7(2)	Au4–Pd–Au1	62.5(2)
Au9–Pd–Au2	123.3(2)	Au4–Pd–I	133.8(2)
Au9–Pd–Au7	63.4(1)	Au1–Pd–I	104.4(2)
Au9–Pd–Au6	69.7(1)	I1–Au1–Pd	173.9(2)
Au9–Pd–Au4	72.3(1)	I6–Au6–Pd	170.5(2)
Au9–Pd–Au1	64.3(2)		
Au9–Pd–I	145.6(2)		
Au5–Pd–Au2	115.2(2)		

at room temperature. This formulation was suggested by FAB-MS and elemental analysis data. The cluster was thought to be neutral by its solubility properties and attempts to form the hexafluorophosphate salt by the addition of $TlPF_6$ were unsuccessful and led to cluster decomposition. This suggested that an iodine atom was bonded directly to the Pd atom. The single crystal X-ray structure analysis confirmed this formulation (*vide infra* and Fig. 1). The ^{31}P NMR spectrum of **1** at room temperature consisted of a single broad peak (δ 45), suggesting fluxional behavior. Rapid skeletal rearrangement of M–Au clusters is a common phenomenon [1, 2]. Upon cooling to −80 °C, the broad signal resolved into a complex spectrum with at least eight multiplet resonances in the range δ 51–42. This behavior suggests the presence of geometric isomers which are rapidly interconverting on the NMR timescale at room temperature. This conclusion is based on the fact that the number and intensities of the peaks at low temperature could not be rationalized from the solid state structure or by any other reasonable single structure.

Compound **1** is an eighteen-electron cluster so it is not expected to react with CO. However, when CO was bubbled through a dichloromethane solution of **1**, a new narrow peak (δ 43.6) appeared in the ^{31}P NMR spectrum. The ^{13}C NMR spectrum of the ^{13}CO labeled product showed three well resolved multiplets (octet, octet, septet) due to coupling with the phosphorus atoms in the CO region at δ 223.8, 220.3, 218.5, respectively, suggesting three CO containing products. The products of this reaction probably result from the substitution of the Pd bound I^- by CO, giving eighteen-electron clusters such as $(CO)Pd(AuPPh_3)_7(AuI)_2{}^+$ and $(CO)Pd(AuPPh_3)_6(AuI)_2$. The second complex results from loss of $(PPh_3)AuI$ and would account for the septet resonance in the ^{13}C NMR spectrum. In accord with this, the conductivity of a dichloromethane solution of **1** under N_2 increased upon exposure to an atmosphere of CO. These CO containing compounds have not been isolated so their identity is speculative. The dissociation of the Pd bound iodide is reasonable, however, since direct halogen to transition metal bonding is unusual in M–Au cluster chemistry. In nearly all cases the halogen atoms are bound only to Au atoms [4, 9].

The reaction of $[Pd(AuPPh_3)_8]^{2+}$ with Br^- in dry acetone solution resulted in the formation of an orange–brown solid in good yield. The FAB-MS of this product was very clean and indicated the parent molecular ion to be $[Pd(AuPPh_3)_7(AuBr)_3]^+$ (**2**). The conductivity of **2**(PF_6) measured in acetonitrile solution was indicative of a 1:1 electrolyte. The ^{31}P NMR spectrum recorded at room temperature was similar to that of **1** in that it consisted of a single broad peak at δ 46 ppm. Upon cooling to −80 °C, the spectrum resolved into three distinct peaks with relative intensities of 2:1:4. The peak intensities are consistent with the presence of seven phosphine ligands as predicted by the FAB-MS data.

Since **2** is a sixteen-electron cluster it should form an eighteen-electron adduct with ligands such as CO.

$$[Pd(AuPPh_3)_8]^{2+} + I^- \longrightarrow \underset{\mathbf{1}}{(I)Pd(AuPPh_3)_7(AuI)_2} \xrightarrow{CO} [(CO)Pd(AuPPh_3)_7(AuI)_2]^+ + \text{other products}$$

$$[Pd(AuPPh_3)_8]^{2+} + Br^- \longrightarrow \underset{\mathbf{2}}{[Pd(AuPPh_3)_7(AuBr)_3]^+} \xrightarrow{CO} \underset{\mathbf{3}}{[(CO)Pd(AuPPh_3)_7(AuBr)_3]^+}$$

$$[Pd(AuPPh_3)_8]^{2+} + Cl^- \xrightarrow{H^+,\ H_2O} \underset{\mathbf{4}}{[Pd(AuPPh_3)_7(AuCl)_3]^+} \xrightarrow{CO} \underset{\mathbf{5}}{[(CO)Pd(AuPPh_3)_7(AuCl)_3]^+}$$

$$[Pd(AuPPh_3)_8]^{2+} + Cl^- \;\text{——}\; \underset{\mathbf{6}}{Pd(AuPPh_3)_8(AuCl)_3} \xrightarrow{CO} \text{no reaction}$$

$$[Pd(AuPPh_3)_8]^{2+} + CN^- \longrightarrow \underset{\mathbf{7}}{Pd(AuPPh_3)_8(AuCN)_3} \xrightarrow{CO} \text{no reaction}$$

Scheme 1.
(All reactions run in acetone solvent.)

A reaction occurred upon the addition of one atm of CO to a dichloromethane solution of **2**, giving two broad peaks at δ 45 and 40 in the room temperature ^{31}P NMR spectrum. This reaction was reversible as the ^{31}P NMR spectrum of **2** returned under a N_2 purge. This reversible behavior has also been observed in the reaction of $[Pd(AuPPh_3)_8]^{2+}$ with CO. When ^{13}CO was used in the reaction, an octet at δ 219 ppm was present in the room temperature ^{13}C NMR spectrum. This suggests that the CO ligand is directly bonded to the Pd atom and, due to fluxionality, the seven PPh_3 ligands appeared equivalent. The IR spectrum of the resulting solid gave $\nu(CO)$ at 1977 cm^{-1}. This is indicative of CO bound to the Pd atom and is shifted in the expected direction (due to less backbonding) from the value of 1955 cm^{-1} observed [10] in $[(CO)Pd(AuPPh_3)_8]^{2+}$. The CO adduct of **2** is therefore the eighteen-electron compound $[(CO)Pd(AuPPh_3)_7(AuBr)_3]^+$ (**3**).

The reaction of $[Pd(AuPPh_3)_8]^{2+}$ with chloride ion gave different products depending on reaction conditions. The cluster formulated as $[Pd(AuPPh_3)_7(AuCl)_3]^+$ (**4**) was prepared by combining $[Pd(AuPPh_3)_8]^{2+}$ and PPNCl in the presence of benzoic acid and wet acetone while the reaction carried out in dry acetone without benzoic acid yielded a neutral cluster formulated as $Pd(AuPPh_3)_8(AuCl)_3$ (**6**). The conductivity of **4** was indicative of a 1:1 electrolyte and the FAB-MS confirmed its formulation. The ^{31}P NMR at room temperature was similar to that of **2** and consisted of a broad resonance at δ 44 which resolved into four distinct multiplets with relative intensity of 2:1:2:2 at −80 °C. The relative intensities are consistent with the presence of seven phosphine ligands. This data confirms that **2** and **4** are bromide and chloride analogues of the same sixteen-electron cluster. In agreement with this, the reaction of **4** with CO gave cluster **5**, which is characterized as the chloride analogue of **3**. The ^{13}C NMR spectrum of **5** consisted of an octet at δ 217 and the $\nu(CO)$ in the IR spectrum was 1979 cm^{-1} in agreement with the formulation.

Clusters **2** and **4** have similar ^{31}P NMR spectra at −80 °C. This suggests that the compounds have the same structure. In **2** the three resonances have relative intensities of 2:1:2 while in **4** there are four resonances with relative intensities of 2:1:2:2. Careful comparison of the spectra suggests that in **2** the higher field resonance of area 4 is probably comprised of two unresolvable peaks of area 2. There are several reasonable structures which can give rise to a 2:1:2:2 pattern but it is impossible to select the best one. A reasonable choice, however, is a structure similar to that of $[(PPh_3)Pt(AuPPh_3)_6(AuCl)_3]$ in the solid state [4] with an $AuPPh_3$ group replacing the PPh_3 ligand. Unfortunately, X-ray quality crystals could not be obtained for **2** or **4**.

The cluster formulated as **6** was first detected as a by-product in the synthesis of $[Pd(AuPPh_3)_8]^{2+}$ and has only been isolated in low yield (15–20%). The ^{31}P NMR spectrum contained two sharp singlets that varied in relative intensity depending on the method of preparation. This can be explained by assuming that two isomers are present. Elemental analysis, FAB-MS and electron counting rules suggested the formulation to be the neutral eighteen-electron cluster $Pd(AuPPh_3)_8(AuCl)_3$ (**6**). In accord with this formulation, **6** did not react with CO. Attempts to obtain X-ray quality crystals have not been successful.

A similar $PdAu_{11}$ cluster was prepared by the reaction of $[Pd(AuPPh_3)_8]^{2+}$ with KCN in methanol/dichloromethane solution. The product isolated is formulated as the neutral eighteen-electron cluster $Pd(AuPPh_3)_8(AuCN)_3$ (**7**). This formulation is based on FAB-MS and solubility data and by analogy to **6**. The ^{31}P NMR of both of these clusters gave sharp lines at room temperature and neither compound reacted with CO. The presence of coordinated cyanide in **7** was confirmed by the observance of $\nu(CN)$ stretches of 2156 and 2144 cm^{-1} in the IR. The only other known M–Au clusters with Au–CN bonds are $[(CN)Pt(AuPPh_3)_8(AuCN)]^+$ and $[(CO)Pt(AuPPh_3)_6(AuCN)_2]$. These compounds have $\nu(CN_{Au})$ stretching frequencies of 2116 and 2115 cm^{-1}, respectively [22].

Crystal structure analysis of (I)Pd(AuPPh$_3$)$_7$(AuI)$_2$ (1)

The solid state structure of **1** consists of well separated molecules. An ORTEP representation of the coordination core is shown in Fig. 1. The geometry of the $PdAu_9$ core is best described as a fragment of a Pd-centered icosahedron (Fig. 2) in accord with its eighteen-electron count. The I atom bound to the Pd is not positioned near an icosahedral vertex but is approximately capping the Au2Au5Au8 triangular face with I–Au contacts of 3.209, 3.109 and 3.410 Å for Au2, Au5 and Au8, respectively. This position minimizes steric contacts with the Au atoms. The Pd–I bond distance of 2.829(6) Å is longer than generally found. Pd–I distances generally range from 2.55 to 2.75 Å for a variety of non-cluster compounds [23]. This lengthening probably results from steric repulsion due to the high coordination number of Pd in the cluster. This is the first example of a direct palladium to halogen bond in a Pd–Au cluster compound. The only other M–Au clusters that contain a direct metal to halogen bond are $[(I)(PPh_3)Pt(AuPPh_3)_4]^+$ and $[(I)(dppe)Pt(AuPPh_3)_4]^+$, but these have not been characterized by X-ray crystallography [9].

The $PdAu_9$ core consists of seven $Au(PPh_3)$ and two AuI groups bonded directly to the central Pd atom. The two AuI units are positioned such that the three iodine atoms are as far apart as possible. These atoms lie on a pseudo mirror plane which contains Pd, Au1, Au5 and Au6 (Fig. 1). It is not clear why the cluster adopts this stereochemistry in the solid state but probably is a result of crystal packing forces. In solution there is evidence for the presence of geometric isomers.

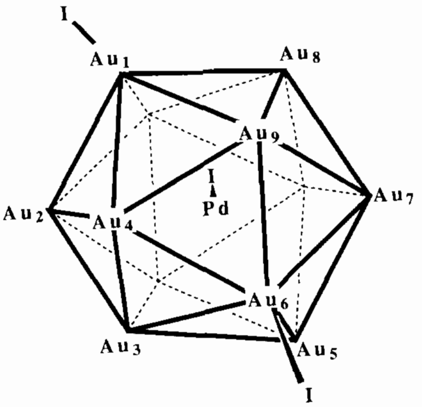

Fig. 2. The metal core geometry of the eighteen-electron cluster **1** shown as a fragment of a centered icosahedron The darkened lines represent bonding interactions between gold atoms. The central Pd atom is bonded to all of the peripheral gold atoms but these bonds are not shown for the sake of clarity. The P atoms of the triphenylphosphine ligands bonded to each Au atom are also not shown

The average Pd–Au and adjacent Au–Au bond distances in **1** are 2.690 Å (range 2.650–2.720 Å) and 2.925 Å (range 2.801–3.316 Å), respectively, and are longer than found in $[Pd(AuPPh_3)_8]^{2+}$ (av. 2.618 and 2.792 Å) [11] and $[(CO)Pd(AuPPh_3)_8]^{2+}$ (av. 2.673 and 2.912 Å) [5]. The average Pd–Au and Au–Au distances increase in the order of increasing Pd coordination number (8, 9 and 10) for $[Pd(AuPPh_3)_8]^{2+}$, $[(CO)Pd(AuPPh_3)_8]^{2+}$ and **1**, respectively.

The average Au–P bond distance of 2.29 Å (range 2.25–2.32 Å) is within the normal range for these types of compounds [1–5, 9–11]. The Au–I bond distances of 2.617(8) and 2.631(5) Å are also within the normal range (2.60–2.69 Å). The Au–PPh_3 vectors are approximately *trans* to the palladium atom (average Pd–Au–P = 167.4°), which is a general trend found in complexes of this type, however, there is a significant deviation in the Pd–Au8–P8 angle (153.6(4)°). The average Pd–Au–P angle not including this value is 169.7°. Significant deviations in these angles have been observed before in crystal structures of such clusters and probably result from crystal packing forces [1–5, 9–11].

Comparison of reactions of 1, $[Pt(AuPPh_3)_8]^{2+}$ and $[Au(AuPPh_3)_8]^{3+}$ with halides

It is interesting to compare the reactions of **1** with X^- (Scheme 1) to those of the analogous sixteen-electron Pt and Au centered clusters. $[Pt(AuPPh_3)_8]^{2+}$ has been shown to react with X^- (X = Cl, Br and I) in acetone solution to give the neutral, eighteen-electron cluster $(PPh_3)Pt(AuPPh_3)_6(AuX)_3$ [4]. The analogous reactions of $[Au(AuPPh_3)_8]^{3+}$ with Cl^- and SCN^- gave $[Au(AuPPh_3)_8(AuX)_2]^+$ and $Au(AuPPh_3)_7(AuSCN)_3$ [25]. All of these reactions involve the fragmentation of the parent cluster and growth leading to the formation of a larger cluster. Larger clusters result because the halide ligand is smaller than the PPh_3 ligand thus permitting more AuL units to fit around the central metal. This phenomenon is well known in gold and mixed metal–gold cluster chemistry [1, 4, 24–26]. In the case of the Pt centered clusters, a PPh_3 ligand is always bound to the Pt thus preventing cluster growth beyond $PtAu_9$. The Pd centered clusters do not have a Pd bound PPh_3 ligand and grow larger to $PdAu_{10}$ and $PdAu_{11}$, with the exception of the iodine containing compound where the Pd bound I atom leads to the formation of a $PdAu_9$ cluster. The Pd bound I presumably has a similar steric effect to the PPh_3 ligand and prevents larger cluster growth. In the case of Au centered clusters the X^- and PPh_3 ligands are only bound to the peripheral Au atoms leading to $AuAu_{10}$ clusters. By this comparison the Pd and Au centered clusters are more similar. The Pt atom has a higher affinity for a PPh_3 ligand and this presumably is the primary reason for the difference in cluster size. Another interesting difference in the chemistry of these halide reactions is that the Pt and Au centered clusters give eighteen-electron products while for Pd centered clusters with $X = Br$ and Cl, the sixteen-electron compounds **2** and **4** result. In accord with the predictions of electron counting rules, clusters **2** and **4** form simple adducts with CO giving **3** and **5**, respectively. The CO ligand in these clusters is labile and quickly dissociates under a N_2 purge. This contrasts with the various CO containing Pt–Au clusters where the CO is irreversibly bound to the Pt atom. The reaction of eighteen-electron M–Au clusters with CO either does not occur or is complicated by loss of ligands bound to the central M (Scheme 1).

Most M–Au cluster compounds show fluxional behavior on the ^{31}P NMR timescale due to rapid skeletal rearrangement of the peripheral gold–phosphine units. The halide derivatives of the Pd, Pt and Au centered clusters discussed above show a marked trend in fluxionality. The Au centered clusters $[Au(AuPPh_3)_8(AuX)_2]^+$ and $Au(AuPPh_3)_7(AuSCN)_3$ are fluxional at all temperatures and show no signs of line broadening at −90 °C. The Pt centered clusters $(PPh_3)Pt(AuPPh_3)_6(AuX)_3$ are rigid at +50 °C, and the Pd centered clusters **1, 2** and **4** have intermediate fluxionality (broad lines at room temperature and rigid at about −80 °C). This trend in fluxionality Au > Pd > Pt probably results from the different strengths of the M–Au bonds.

Schoondergang *et al.* have discussed ideas on a mechanism for the fragmentation and growth reaction of $[Pt(AuPPh_3)_8]^{2+}$ with halides [4]. Some of the important steps are shown below. The first step is initiated by addition of X^- to the sixteen-electron cluster $[Pt(AuPPh_3)_8]^{2+}$ with elimination of PPh_3AuX.

$$[Pt(AuPPh_3)_8]^{2+} + X^- \longrightarrow [Pt(AuPPh_3)_7]^+ + PPh_3AuX \qquad (1)$$

$$PPh_3AuX \longrightarrow PPh_3 + AuX \qquad (2)$$

$$[Pt(AuPPh_3)_7]^+ + PPh_3 \longrightarrow [(PPh_3)Pt(AuPPh_3)_7]^+ \qquad (3)$$

$$[(PPh_3)Pt(AuPPh_3)_7]^+ + X^- \longrightarrow (PPh_3)Pt(AuPPh_3)_6(AuX) + PPh_3 \qquad (4)$$

Growth to the product $(PPh_3)Pt(AuPPh_3)_6(AuX)_3$ is complicated and could involve reactions such as shown in step (5).

$$[(PPh_3)Pt(AuPPh_3)_6(AuX) + 2AuX \longrightarrow (PPh_3)Pt(AuPPh_3)_6(AuX)_3 \qquad (5)$$

In the case of the Pd centered clusters the equilibrium position of some of these steps is changed to give the observed products. For example, if steps (3) and (4) are unfavorable all that is needed to form **2** and **4** is the addition of three equivalents of AuX to $[Pt(AuPPh_3)_7]^+$. The formation of **1** could result from the addition of one equivalent of I^- and two of AuI to $[Pt(AuPPh_3)_7]^+$. Although this mechanism is speculative, it can be useful in the prediction of new reactions.

Supplementary material

Table 1 (listing the complete crystal data and data collection parameters for **1**), and Tables 2–5 (listing general temperature factor expressions, final positional and thermal parameters for all atoms, and distances and angles) (22 pages) are available from the authors on request.

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