though some qualitative observations have been reported.[28b,29]

Thermolysis experiments, under flowing Ar, show that the Ph_4P^+ salt of I does not show any appreciable weight loss below 350 °C. Its decomposition is smooth and continuous and is complete at 536 °C. The final product was unequivocally identified by its X-ray powder diffraction pattern as β-In_2Se_3.[30] This behavior is not shared by the Et_4N^+ and Pr_4N^+ salts, which, although they begin to decompose at lower temperature, convert to β-In_2Se_3 via intermediate, Se-rich phases. Further studies on the thermolysis of these compounds are in progress.

Acknowledgment. We thank Dr. Don Ward for assistance in the X-ray data collection and structure solution. Financial support from the Center for Fundamental Materials Research at Michigan State University and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Professor Ibers for bringing ref 9b to our attention.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms in the anion (7 pages); a listing of calculated and observed ($10F_o/10F_c$) structure factors (43 pages). Ordering information is given on any current masthead page.

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Heterobimetallic Au-Pd Phosphine Cluster Complexes. X-ray Crystal and Molecular Structure of $[Au_8Pd(PPh_3)_8](NO_3)_2$

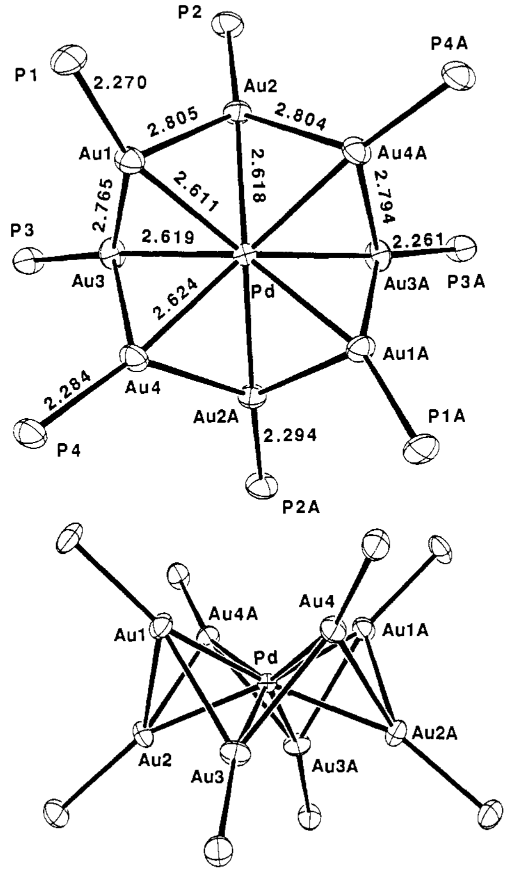

Figure 1. ORTEP drawings (two views) of the coordination core of the cation of **1** with selected bond distances (Å). Ellipsoids are drawn with 50% probability boundaries. Phenyl rings have been omitted for clarity. Atoms with the "A" label are related to their counterparts, e.g., Au4A and Au4, by a crystallographic C_2 axis that passes through the Pd atom. Selected angles (deg) are as follows, wherein numbers refer to respective Au atoms: Pd-1-P1 = 153.6 (2); Pd-2-P2 = 160.3 (2); Pd-3-P3 = 164.1 (2); Pd-4-P4 = 163.5 (2); 1-Pd-1A = 132.7 (1); 1-Pd-2 = 64.88 (5); 1-Pd-2A = 135.93 (4); 1-Pd-3 = 63.83 (5); 1-Pd-3A = 145.11 (4); 1-Pd-4 = 74.80 (6); 1-Pd-4A = 88.71 (7); 2-Pd-2A = 137.0 (1); 2-Pd-3 = 77.14 (7); 2-Pd-3A = 82.92 (7); 2-Pd-4 = 133.42 (5); 2-Pd-4A = 64.68 (5); 3-Pd-3A = 123.6 (1); 3-Pd-4 = 64.39 (5); 3-Pd-4A = 140.09 (5); 4-Pd-4A = 138.5 (1). Average esd's for Au-Pd, Au-Au, and Au-P distances are 0.002, 0.002, and 0.007, respectively.

A large number of transition-metal-gold cluster compounds have been prepared containing transition metals such as V, Cr, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Pt, and Ag.[1-12] There have not, however, been any reports of well-characterized compounds containing Au-Pd bonds.[13-15] Because Pd is a catalytically important metal and gold-palladium heterogeneous catalysts are known and used commercially for oxidation catalysis,[16-18] and because we are interested in developing a better understanding of the role of Au in bimetallic catalysis,[19-26] we have devoted a

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considerable effort to the synthesis and isolation of cluster compounds containing Pd and Au. We report here the synthesis and characterization, including a single-crystal X-ray crystallographic analysis, of the first palladium–gold cluster compound.

Various synthetic strategies have been used to prepare transition-metal–gold phosphine cluster compounds.[1] These methods include (i) the reaction of transition-metal hydrides with the $Au(PPh_3)^+$ moiety, (ii) the reaction of PPh_3 with known transition-metal–gold clusters, and (iii) the reaction of CO or H_2 with various transition-metal complexes in the presence of $Au(PPh_3)NO_3$. This latter strategy has been used for the synthesis of platinum–gold cluster compounds[1,7] and also for the preparation of gold cluster compounds,[1] but it proved ineffective for palladium–gold cluster compounds.

$[Au_8Pd(PPh_3)_8]^{2+}$ (**1**) was made by the reaction of a CH_2Cl_2 solution of $Pd(PPh_3)_4$[27] and 3 equiv of $Au(PPh_3)NO_3$ with a MeOH solution of 2 equiv of $NaBH_4$ at room temperature.[28] After the reaction was quenched with water, a dark purple solid was isolated. This reaction produced $[Au_8Pd(PPh_3)_8]^{2+}$ (**1**) as the major product, which was separated from a minor product identified as $[Au_6Pd(PPh_3)_7]^{2+}$ (**2**), vide infra, by HPLC using an 85% ethanol/15% 0.125 M NH_4NO_3 isocratic elution.[28] Dark platey purple crystals of the nitrate salt of **1** were obtained in 52% yield from a $MeOH-(C_2H_5)_2O$ solvent mixture.

A crystal of the nitrate salt of **1** was subjected to a single-crystal X-ray analysis.[29] The structure of the coordination core with selected distances and angles is shown in Figure 1. The structure of **1** consists of eight $Au(PPh_3)$ units bonded to a central Pd atom. The metal atoms form a centered-crown structure essentially the same as the structure of $[Au_8Pt(PPh_3)_8](NO_3)_2$,[7] which was described as a centered square antiprism that has undergone distortion perpendicular to the S_8 axis such that the connections in the squares are nonbonding.

The core structure of **1**, however, is slightly contracted as compared to that of the Au_8Pt complex. For example, the Au–Au bond distances in **1** (average 2.792 (2) Å, range 2.765–2.8048 Å) are slightly shorter than the Au–Au distances in $[Au_8Pt(PPh_3)_8](NO_3)_2$ (average 2.827 (2) Å, range 2.800–2.864 Å)[7] and are within the range of values observed in other transition-metal–gold cluster compounds containing primarily phosphine ligands (2.593–3.222 Å).[1] The Au–Pd distances in **1** (average 2.618 (2) Å, range 2.611–2.624 Å) are also slightly shorter than the Au–Pt distances (average 2.635 Å, range 2.631–2.640 Å);[7] the magnitude of this difference is comparable to the magnitude of the difference in covalent radii between Pd and Pt.

The Au–P distances in **1** (average 2.275 (7) Å, range 2.261–2.294 Å) are very similar to those in $[Au_8Pt(PPh_3)_8](NO_3)_2$ (average 2.268 Å, range 2.251–2.288 Å).[7] The Au–PPh_3 vectors in both **1** and the Au_8Pt complex are approximately trans to the transition-metal atom (average Pd–Au–P = 160.4 (2)°, average Pt–Au–P = 161.7 (4)°), which is a general trend seen in complexes of this type.[1] The Au–M–Au bond angles are also very similar in the two compounds (average Au–Pd–Au = 64.5 (5)° in **1**, average Au–Pt–Au = 64.9° in $[Au_8Pt(PPh_3)_8](NO_3)_2$).

Least-squares plane calculations also show that the structures of the two complexes are very similar.[30] As shown in Figure 1, the two planes containing the gold atoms, [Au1, Au4, Au1A, Au4A] and [Au2, Au3, Au2A, Au3A], are parallel in **1** and in the Au_8Pt complex. The distances between the transition-metal atom and these two planes are also very similar. The distance between plane [1, 4, 1A, 4A] and the metal is 0.99 Å in the Pd complex and 1.02 Å in the Pt complex, and the distance between plane [2, 3, 2A, 3A] and the metal is 1.11 Å in both complexes.

The solution NMR spectroscopic data for **1** is entirely consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR spectrum recorded at room temperature with CH_2Cl_2 as solvent consisted of a singlet at δ 48.8. ^1H NMR spectroscopy showed no evidence of any hydride ligands.

Positive ion FABMS analysis of the PF_6^- salt of **1** gave a spectrum with well-resolved peaks. An analysis of the isotopic ion distribution pattern for the highest mass peak gave a most abundant mass ion of 3923.5. A complete simulation of all isotopic combinations for $[Au_8Pd(PPh_3)_8PF_6]^+$ gave an isotopic ion distribution pattern that closely matched the observed pattern, and a calculated value of m/z 3924 for the most abundant ion. An analysis of the fragmentation pattern [3778 $(M - PF_6)^+$, 3663 $(M - PPh_3)^+$, 3517 $(M - PPh_3 - PF_6)^+$, 3399 $(M - 2PPh_3)^+$] suggests that the neutral compound is $[Au_8Pd(PPh_3)_8](PF_6)_2$.

Although the nitrate counterions were not located and refined in the X-ray crystal structure analysis due to their severe disorder, the FABMS analysis supports the formulation of the Au_8Pd complex as a dication. Also, the conductivity of 166.2 cm^2 mho mol^{-1} is indicative of a 1:2 electrolyte in CH_3CN solution.

Complex **2** was characterized as $[Au_6Pd(PPh_3)_7]^{2+}$ by $^{31}P\{^1H\}$ NMR spectroscopy (CH_2Cl_2, 25 °C): δ 47.5 (d, J_{P-P} = 31 Hz, intensity 6), 59.8 (m, J_{P-P} = 31 Hz, intensity 1). The doublet at δ 47.5, with an intensity of 6 relative to that of the peak at δ 59.8, is assigned to the $Au(PPh_3)$ ligands. The multiplet at δ 59.8 is an odd-line pattern suggestive of a septet, which indicates the presence of six equivalent $Au(PPh_3)$ units on the NMR time scale, and is assigned to $Pd(PPh_3)$. ^1H NMR spectroscopy showed no evidence for any hydride ligands. Preliminary FABMS results support the formulation of **2** as stated. Further evaluation of the structure and reactivity of **2** is presently under way.

$[Au_8Pd(PPh_3)_8(CO)](NO_3)_2$ (**3**) was prepared by the exposure of a solution of **1** to 1 atm of CO with use of CH_2Cl_2 as solvent.[31]

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(28) $[Au_8Pd(PPh_3)_8]^{2+}$ (**1**) and $[Au_6Pd(PPh_3)_7]^{2+}$ (**2**) were isolated as the nitrate salts from the same reaction. A 100-mL Schlenk flask was charged with $Pd(PPh_3)_4$ (600 mg, 5.19 × 10^{-1} mmol), $Au(PPh_3)NO_3$ (813 mg, 1.56 mmol), and a magnetic stir bar. Dichloromethane (40 mL) was added to the reaction vessel, and a dark red homogeneous solution resulted. A methanol solution of $NaBH_4$ (30 mL, 44 mg, 1.16 mmol) was added to the magnetically stirred reaction mixture, during which time gas evolution occurred and a gold-colored solid precipitated from the solution. The dark brown solution was stirred at ambient temperature for 10 min, at which time water (1 mL) was added to the reaction mixture to quench the reaction. The solvents were removed under vacuum. Methanol (20 mL) was added to the flask, and the crude mixture was filtered through diatomaceous earth to remove the gold-colored precipitate. The dark brown filtrate was reduced in volume to 5 mL, and diethyl ether (40 mL) was added to precipitate a dark purple solid. The solid was isolated on a fritted filter, washed with diethyl ether (40 mL), and dried under vacuum. $[Au_8Pd(PPh_3)_8]^{2+}$ (**1**) was separated from $[Au_6Pd(PPh_3)_7]^{2+}$ (**2**) by HPLC using an 85% ethanol/15% 0.125 M NH_4NO_3 isocratic elution (degassed under helium; flow rate = 10 mL/min; Rainin Dynamax Macro 60-Å 8-μm C-18 reverse-phase column, 21.4 mm i.d. × 25 cm). Retention times: (**1**) 5.8 min; (**2**) 5.2 min. Upon collection of the two fractions, each was evaporated to dryness, and the cluster was extracted with CH_2Cl_2 (5 mL). The solution was filtered through diatomaceous earth, rinsed with 5–10 mL of CH_2Cl_2, and again evaporated to dryness. Crystals of the nitrate salt of **1** were grown by dissolving the extracted solid in a minimal amount of methanol and adding diethyl ether in small portions, with mixing of the solution, until a small amount of a fine microcrystalline precipitate formed. The flask was left undisturbed overnight during which time dark platey purple crystals formed. Yield: 399 mg (52.4%, based on Au, after recrystallization). The compound is soluble in alcohols, dichloromethane, chloroform, and acetone and insoluble in saturated hydrocarbons and diethyl ether; it is air-, light-, and moisture-stable both in the solid state and in solution. The PF_6^- salt of **1** was made by dissolving **1** (50 mg, 0.0128 mmol) in methanol (2 mL) and adding the solution dropwise to a stirred solution containing NH_4PF_6 (21 mg, 0.129 mmol) in methanol (10 mL). Immediately upon mixing of the solution, a brown precipitate formed, which was then collected on a fritted-glass filter, washed with methanol (10 mL), and dried under vacuum. Anal. Calcd for $Au_8PdP_{10}C_{144}H_{120}F_{12}$, $[Au_8Pd(PPh_3)_8](PF_6)_2$: C, 42.49; H, 2.97; Au:Pd ratio = 8; Au:P ratio = 0.8. Found: C, 41.90; H, 2.90; Au:Pd ratio = 7.39; Au:P ratio = 0.78.

(29) Details of experimental procedures are included as supplementary material. The crystal of **1** was unstable upon removal from the solvent and therefore was coated with a viscous high-molecular-weight hydrocarbon and secured on a glass fiber by cooling to −86 °C. Compound **1** crystallized in the monoclinic space group $C2/c$: a = 17.06 (1) Å, b = 36.66 (2) Å, c = 25.02 (2) Å, β = 98.43 (5)°, V = 15476 (28) Å^3, Z = 4, d_{calc} = 1.676 g cm^{-3}, and R = 0.053 for 5268 observed reflections [$2\theta_{max}$ = 42°, $F_o^2 > 3\sigma(F_o^2)$].

(30) Steggerda, J. J. Personal communication.

The characterization data are consistent with the formulation of **3** as the carbonyl adduct of **1** with one CO ligand bonded to the Pd atom. This reaction is analogous to the reaction of $[Au_8Pt(PPh_3)_8](NO_3)_2$ with CO, which yielded $[Au_8Pt(PPh_3)_8(CO)](NO_3)_2$.[6] The $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2, 25 °C) of **3** showed a single resonance at δ 44.5 (singlet). The ^{13}C NMR solution spectrum (CD_2Cl_2, 25 °C) of isotopically labeled $[Au_8Pd(PPh_3)_8(^{13}CO)](NO_3)_2$ complex consisted of a multiplet of seven well-resolved lines not inconsistent with a nonet pattern where the wing resonances are in the noise centered at δ 229.7 ($J_{^{13}C-P}$ = 11.7 Hz). The IR spectrum (KBr) of **3** displayed a $\nu(CO)$ absorption at 1955 cm^{-1}, which is consistent with a terminally bound metal carbonyl. The $\nu(CO)$ absorption shifted to lower energy (1919 cm^{-1}) in the IR spectrum when **3** was synthesized with 99% ^{13}CO. The conductance of **3** in CH_3CN showed it to be a 1:2 electrolyte.

Preliminary results indicate that this class of cluster compounds possesses a rich chemistry. We are presently studying these complexes with respect to their catalytic potential, their reactivity with small molecules, and their reactivity with other transition-metal cations in an attempt to synthesize trimetallic clusters. For example, in addition to the reaction with CO, we have discovered that complex **1** reacts with MeI and $AgNO_3$.

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Supplementary Material Available: Experimental details of the X-ray structure determination, Figures S1 and S2, displaying PLUTO drawings (two views) of **1**, and Tables I–VI, listing crystal structure data collection and refinement parameters, final positional and thermal parameters for all atoms including calculated hydrogen positions, distances and angles, least-squares planes, and general temperature factor expressions (27 pages); Table VII, listing observed and calculated structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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(31) $[Au_8Pd(PPh_3)_8(CO)](NO_3)_2$ (**3**) was prepared by dissolving complex **1** (100 mg, 2.56 × 10^{-2} mmol) in 10 mL of dichloromethane and placing the solution under 1 atm of CO. The color of the solution changed from purple to dark brown immediately. The volume of the solution was reduced to 2 mL and transferred to a flask containing 60 mL of diethyl ether. The brown precipitate was collected on a fritted filter, washed with 40 mL of diethyl ether, and dried under vacuum. Yield: 98 mg (97%). It is soluble in alcohols, dichloromethane, chloroform, and acetone and insoluble in saturated hydrocarbons and diethyl ether; it is air-, light-, and moisture-stable both in the solid state and in solution. The isotopically labeled analogue, $[Au_8Pd(PPh_3)_8(^{13}CO)](NO_3)_2$, was prepared by the same procedure using ^{13}CO.

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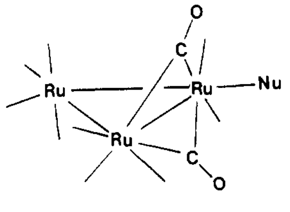
Nucleophilic Activation of Metal Carbonyl Clusters.[1] Isolation and Structure of the Elusive Chloride Adduct $Ru_3(CO)_{11}Cl^-$

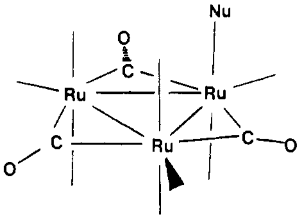
Homogeneous catalysts based on metal carbonyls often employ anionic nucleophile promoters;[2] e.g., halides are used as promoters in catalysis by the prototype cluster $Ru_3(CO)_{12}$.[3,4] While the roles of such promoters are yet to be fully delineated, Kaesz,[5] Gladfelter,[6] and others[7] have shown facile nucleophilic attack of halides and other anions on $Ru_3(CO)_{12}$ in certain media to result in CO labilization to give anionic clusters $Ru_3(CO)_mX_n^{n-}$. Recently, Han et al.[8] described reversible transformations for some products from reactions of $Ru_3(CO)_{12}$ plus the salts [PPN]Nu (PPN^+ = $(Ph_3P)_2N^+$; Nu^- = Cl^-, Br^-, I^-) in tetrahydrofuran. On the basis of in situ spectroscopic evidence, the initial cluster product with Cl^- (eq 1) was proposed to have the stoichiometry $Ru_3(CO)_{11}Cl^-$

$$Ru_3(CO)_{12} + Cl^- \rightarrow Ru_3(CO)_{11}Cl^- + CO \qquad (1)$$

and a structure such as illustrated by A. However, attempts to isolate this anionic cluster[8] or analogous triruthenium products with other anions[6,7c] have been frustrated by the apparent instability of the $Ru_3(CO)_{11}Nu^-$ species. Described here is the successful isolation and structural characterization of one example of this key intermediate, the unstable salt $[PPN][Ru_3(CO)_{11}Cl]$ (I). In this case the cluster anion is shown to have the configuration B, different from that proposed.



A



B

A solution of I was prepared by adding 10 mL of deaerated THF to a nearly equimolar mixture of the two solids [PPN]Cl (0.062 g, 0.10 mmol) and $Ru_3(CO)_{12}$ (0.058 g, 0.09 mmol) under CO in a Schlenk tube. After 30 min of stirring, all the solid had dissolved and the initially orange solution had turned to a deep red color. The THF was then removed by evaporation under vacuum to leave a dark red solid residue. A CO atmosphere was reintroduced into the Schlenk tube, and a minimal amount of diethyl ether was added (under CO) to redissolve the solid. The resulting dark red solution was then transferred via syringe and under CO to the inner chamber of a special Schlenk tube modified for recrystallization via the solvent vapor-exchange method.[9] Hexane, deaerated by entraining with CO, was added via syringe to the outer chamber of the same apparatus, and the system was left undisturbed for several hours while dark red crystals formed with size and quality suitable for single-crystal X-ray structure determination. The elemental analysis of the recrystallized adduct was shown to be consistent with the formulation $[PPN][Ru_3(CO)_{11}Cl]$.[10]

The FTIR spectrum of I when redissolved in THF under CO gave ν_{CO} bands at 2060 s, 2026 vs, 2009 s, 1975 m, 1962 m, and 1828 s, br cm^{-1}. The only substantive difference between this

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(1) Reported initially at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988.

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(10) Elemental analysis was performed by Galbraith Laboratories. Calcd for $C_{47}H_{30}O_{11}NP_2ClRu_3$: C, 47.62; H, 2.55; N, 1.18; Cl, 2.99. Found: C, 46.60; H, 2.64; N, 1.14; Cl, 2.99.

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