X-ray Photoelectron Spectroscopy of a Series of Heterometallic Gold–Platinum Phosphine Cluster Compounds

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Introduction

An extensive series of heterobimetallic gold–platinum cluster complexes of the general formulation $[(L)_yPt(AuPPh_3)_x(ML)]^{n+}$ where L = ligand (such as PPh_3, halide, H, RNC, or CN), M = metal (Au or Hg), x = 2–8, and n = 1 or 2 have recently been reported.[1-7] These $PtAu_x$ clusters have shown a variety of novel structures and interesting reactivity.[1-11] Mixed-metal clusters of this type are of potential importance in many areas. For example, such clusters may serve as models for bimetallic surface catalysts or as supported catalyst precursors themselves.[12-14] Some of these clusters have been shown to be excellent catalysts for the equilibration of H_2 and D_2 and to reversibly bind molecular H_2.[15] In order to better understand the electronic structure, charge distribution, and reactivity of these novel materials, as well as to develop physical methods to study larger clusters and supported clusters, an X-ray photoelectron spectroscopy (XPS) study was undertaken. Although there have been XPS studies of phosphine-stabilized gold clusters,[16-18] there have been no reports on ligand stabilized mixed-metal platinum–gold cluster compounds.

Experimental Section

All of the compounds listed in Table I were prepared and characterized according to literature methods: cluster **1**,[7] **2**,[6] **3**,[6] **4**,[4,5] **5**,[2] **6**,[19] **7**,[2] **8**,[3] **9**,[2] **10**,[2] **11**,[2] **12**,[2] **13**,[20] and **14**.[21] Samples were prepared for XPS investigation by supporting them on a thin layer of treated Al support. The Al foil was pretreated by polishing and then oxidizing in air at 50 °C for 30 min. This process produces a layer of Al_2O_3 about 40 Å thick, which minimizes chemical interaction between the clusters and the Al foil. XPS spectra were recorded using a Varian IEE-15 instrument employing Mg $K\alpha_{1,2}$ radiation ($h\nu$ = 1253.6 eV). All experiments were carried out at a pressure of approximately 1×10^{-6} Torr. Usual procedures were used for calibrating the energetic scale.[22]

Two regimes of the β-analyzer were used for recording XPS spectra. For regime I the resolution of the analyzer measured as the full width at the half-maximum (fwhm) of the Au $4f_{7/2}$ peak from metallic gold was 1.16 eV, and for regime II the corresponding value was 1.60 eV. Regime I was used for recording the most intense lines (Au 4f and C 1s), while regime II was used for the other lines. The spectrometer pass energies for regimes I and II were 50 and 100 eV, respectively. The C 1s line (285.00 eV) from the triphenylphosphine (PPh_3) ligands was used as the internal standard.

Results and Discussion

Internal Standard. The XP (C 1s) spectra for phosphine ligands are different from the corresponding spectra for hydrocarbon contamination on the surface of metallic gold (Figure 1 of the supplementary material[23]). The characteristic satellite peaks were observed on the C 1s spectra of compounds with phosphine ligands. The appearance of this satellite is due to π–π^* transfer in the phenyl rings. The probability of excitation of this transfer, measured as the ratio of the intensity of the satellite peak to the intensity of the C 1s peak, is equal to approximately 0.06. The energy of this transfer (the difference between the maxima of the satellite and main peak) is 6.7 ± 0.1 eV. The fwhm values of the C 1s main lines are shown in Table I. There is not an obvious trend in these values, as might be expected, since some of the clusters contain phosphine ligands bound to different metals. All of the C 1s peaks are relatively sharp and therefore can be used as an internal standard. This is a traditional and reliable method of internal referencing. It is also noted that the E_b of Au in the clusters is independent of sample thickness.

In order to verify the reliability of using the C 1s peak as a calibration peak, we have obtained the XP spectra for two compounds, $[(AuPPh_3)_8](NO_3)_2$ and $(I)Pd(AuPPh_3)_7(AuI)_2$,[24] on a PHI-551 spectrometer. This instrument differs from the Varian IEE-15 spectrometer by having a higher base vacuum ($\sim 10^{-10}$ Torr) and a higher density of excited photons on one unit of the surface of the sample under study. It was established that the positions of the photoelectron peaks for these compounds were identical on both instruments. It should be noted that E_b(C 1s) = 285.0 eV attributed to the peak of the carbon contamination on the surface of metallic gold gives E_b(Au $4f_{7/2}$) = 84.2 eV for metallic gold under our experimental conditions.

Nature of Gold in the Cluster Compounds. The Au $4f_{7/2}$ E_b's in all cluster compounds (range 84.57–85.07 eV) are shifted to

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Table I. XPS Data for Cations of the Pt–Au Cluster Compounds and Comparison with Data for Other Compounds

no.	compound	Au $4f_{7/2}$ E_b, eV	fwhm Au $4f_{7/2}$	fwhm C 1s	Pt $4f_{7/2}$ E_b, eV	P 2p E_b, eV	N 1s E_b, eV	S_1/S_2[a]	ref
1	$[(CN)Pt(AuPPh_3)_8(AuCN)]NO_3$	84.57	1.51	1.45	72.8[b]	131.6	397.8	0.19	*f*
2	$[(CNR^c)Pt(AuPPh_3)_8](NO_3)_2$	84.63	1.35	1.45	72.8	131.7	399.2	0.20	*f*
3	$[Pt(AuPPh_3)_8](NO_3)_2$	84.60	1.43	1.40	72.0	131.6		0.20	*f*
4	$[(PPh_3)(H)Pt(AuPPh_3)_7](NO_3)_2$	84.92	1.30	1.37	72.1	131.8		0.23	*f*
5	$[(PPh_3)Pt(AuPPh_3)_5(HgNO_3)_2]NO_3$	84.85	1.53	1.32	72.5	131.7	406.3	0.26	*f*
6	$[(PPh_3)Pt(AuPPh_3)_6(HgNO_3)]NO_3$	84.77	1.57	1.43	72.2	131.6	406.2	0.23	*f*
7	$[(PPh_3)(CN)Pt(AuPPh_3)_6]NO_3$	84.70	1.60	1.40	72.5	131.8	398.1	0.24	*f*
8	$[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$	84.88	1.47	1.33	72.1	131.7		0.24	*f*
9	$[(PPh_3)(CO)Pt(AuPPh_3)_5]Cl$	84.57	1.52	1.42	72.5	131.6		0.26	*f*
10	$[(dppe)Pt(AuPPh_3)_4](PF_6)_2$	85.07	1.67	1.47	72.8	131.8		0.29	*f*
11	$[(I)(PPh_3)Pt(AuPPh_3)_4]BF_4$	84.77	1.87	1.53	72.2	131.7	619.1[d]	0.26	*f*
12	$[(PPh_3)_2Pt(AuPPh_3)_3]PF_6$	84.88	1.67	1.55	72.2	131.8		0.36	*f*
13	$[(\mu\text{-}CO)_3(PPh_3)_4Pt_3(AuPPh_3)]NO_3$	84.97	1.71	1.42	72.7	131.6		2.12	*f*
14	$[Au_8(PPh_3)_8](NO_3)_2$	84.67	1.60	1.37		131.7			*f*
15	$Au(PPh_3)NO_3$	85.37	2.11	1.53		132.0	406.6		*f*
16	$Au(PPh_3)Cl$	85.55	2.07	1.70		132.0	198.8[e]		*f*
17	Au metal	84.20	1.16	1.80					*f*
18	$Pt(PPh_3)_4$				71.7	131.5			*f, g*
19	$Pt(PPh_3)_2Cl_2$				73.5	131.6	198.1		*g*
20	K_2PtCl_4				73.3		199.3		*f*

[a] S_1/S_2 is the intensity ratio for [Pt $4f_{7/2}$]/[Au $4f_{7/2}$] (see text and supplementary material). [b] Wide peak (±0.2 eV). [c] R = 2,6-dimethylphenyl. [d] I $3d_{5/2}$. [e] Cl 2 p. [f] This work. [g] Reference 26.

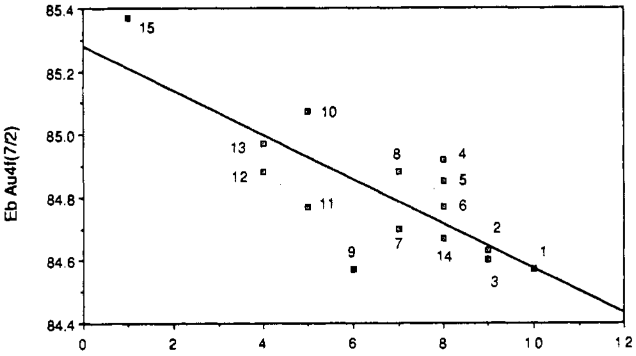

Figure 1. Binding energy of Au $4f_{7/2}$ for Pt–Au clusters as a function of the total number of metal atoms, N. The numbers of the points correspond to the compound numbers in Table I.

higher values compared to that of metallic gold (84.20 eV for Au(0)) but are lower than in $AuPPh_3NO_3$ and $AuPPh_3Cl$ (85.37 and 85.55 eV for Au(I)) and lie in the same range found for gold cluster compounds examined previously.[16–18] The *Eb*'s for $AuPPh_3NO_3$ and $AuPPh_3Cl$ are close to the value reported for $AuPPh_3I$ (85.6 eV).[17,18] The Au $4f_{7/2}$ E_b's for all of the cluster compounds are close, which indicates that the Au atoms have similar electron densities. These results show that the effective charge of Au in the cluster compounds is between those of Au(0) and Au(I) and that the E_b of Au $4f_{7/2}$ is determined primarily by the gold–phosphine and gold–gold interactions.

The dependence of the Au $4f_{7/2}$ E_b on the number of metal atoms in the cluster (N) is presented in Figure 1. In general, E_b decreases with increasing N. This is the same trend as observed with supported, naked metal clusters,[25] but the data points in the figure show a larger spread from the least-squares line. This is most likely due to the fact that the compounds under study differ from each other not only in number of metal atoms but also in structure, number, and type of ligands and in charge. It should be noted in the figure that the cluster cations with the largest negative deviation in E_b from the least-squares line are ones with 1+ charge, while the 2+ charged clusters generally show a positive deviation. This dependence of the Au $4f_{7/2}$ E_b on the magnitude of the positive charge of the cluster cation is expected and has been previously noted for gold clusters.[17,18]

The Au $4f_{7/2}$ fwhm values for the Pt-centered cluster compounds average 1.54 eV (range 1.30–1.87 eV) and are smaller than values reported for gold clusters such as $[Au_9(PPh_3)_8](NO_3)_2$ (1.8 eV) and $[Au_{11}(PPh_3)_7I_3]$ (1.9 eV).[17,18] These gold clusters are gold-centered, however, and may be expected to give different E_b's for the central and peripheral gold atoms. The XP spectrum of the cluster $[Au_8(PPh_3)_8]^{2+}$ has been previously reported,[17,18] and although the Au $4f_{7/2}$ E_b values (84.9 and 84.7 eV for ClO_4^- and pic$^-$ salts, respectively) agree well with the value measured here (84.63 eV), the Au $4f_{7/2}$ fwhm is significantly larger (1.9 compared with 1.57 eV measured here). In this cluster, all of the Au atoms are bonded to a PPh_3 ligand, so the previously reported large Au $4f_{7/2}$ fwhm values must be at least in part due to the XPS instrument and sample preparation methods. Our fwhm value, however, agrees well with that reported by van Attekum (1.5 ± 0.1 eV).[16] Although it is tempting to try to correlate the Au $4f_{7/2}$ fwhm values for the Pt-centered clusters with structure, specifically the number of different Au environments, our data reflect no obvious trend.

Nature of Platinum in the Cluster Compounds. The Pt $4f_{5/2}$ peak of the platinum-centered cluster compounds is partialy overlapped by the $K\alpha_{3,4}$ satellite of the Au 4f line. Fortunately, the Pt $4f_{7/2}$ peak is observed relatively far from the position of this satellite, so we can accurately determine the position of this peak. The XP spectrum in the region of these lines for $[(PPh_3)(H)Pt(AuPPh_3)_7](NO_3)_2$ is shown in Figure 2 of the supplementary material.[23] For the exact identification of the Pt $4f_{7/2}$ peak and for comparison purposes, we recorded the XP (Pt $4f_{7/2}$) spectra for $Pt(PPh_3)_4$ (Pt(O), E_b = 71.7 eV in agreement with the literature[26]) and K_2PtCl_4 (Pt(II), E_b = 73.3 eV). E_b for metallic platinum (Pt(O)) is 71.3 eV.[27,28] The nature of the ligand bound to Pt has a strong influence on the electron density and hence the effective charge of Pt.[26] For the clusters examined here, we also see a significant effect. For example, the isonitrile derivative $[(CNR)Pt(AuPPh_3)_8](NO_3)_2$ (E_b = 72.8 eV) has an effective charge close to that of Pt(II) in comparison to $[Pt(AuPPh_3)_8](NO_3)_2$ (E_b of 72.0 eV), whose charge is between that of Pt(O) and Pt(II). The cluster compounds which contain π-acceptor ligands on Pt (compounds **1**, **2**, **7**, **9**, and **13**; average E_b = 72.7 eV) also have higher Pt $4f_{7/2}$ E_b's than the other Pt-

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Table II. Hg XPS Data for Pt–Au–Hg Cluster Compounds and Comparison with Data for Other Hg Compounds

compound	Hg $4f_{7/2}$ E_b, eV	ref
$[(PPh_3)Pt(AuPPh_3)_5(HgNO_3)_2]NO_3$	100.5	*a*
$[(PPh_3)Pt(AuPPh_3)_6(HgNO_3)]NO_3$	100.3	*a*
$[Hg_2(H_2O)_2](NO_3)_2$	101.4	*b*
Hg metal	99.2	*c*

[a] This work. [b] Reference 32. [c] Reference 37.

Table III. XPS Data for Anions of the Pt–Au Cluster Compounds and Comparison to Data for Simple Salts

	E_b, eV				
compound	(NO_3) N 1s	F 1s	P 2p	Cl 2p	ref
$[(CN)Pt(AuPPh_3)_8(AuCN)]NO_3$	406.0				*c*
$[(CNR^a)Pt(AuPPh_3)_8](NO_3)_2$	406.2				*c*
$[Pt(AuPPh_3)_8](NO_3)_2$	406.2				*c*
$[(PPh_3)(H)Pt(AuPPh_3)_7](NO_3)_2$	406.2				*c*
$[(PPh_3)Pt(AuPPh_3)_5(HgNO_3)_2]NO_3$	406.3				*c*
$[(PPh_3)Pt(AuPPh_3)_6(HgNO_3)]NO_3$	406.2				*c*
$[(PPh_3)(CN)Pt(AuPPh_3)_6]NO_3$	406.3				*c*
$[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$	406.1				*c*
$[Au_8(PPh_3)_8](NO_3)_2$	406.3				*c*
$[(\mu\text{-}CO)_3(PPh_3)_4Pt_3(AuPPh_3)]NO_3$	406.0				*c*
KNO_3	407.6				*d*
$[Hg_2(H_2O)_2](NO_3)_2$	407.2				*e*
$[(I)(PPh_3)Pt(AuPPh_3)_4]BF_4$		685.4			*c*
$[Pt_2(CNCH_3)_6]BF_4$		685.8			*f*
$[RuCl(NO)_2(PPh_3)_2]BF_4$		686.6			*g*
$[(PPh_3)(CO)Pt(AuPPh_3)_5]Cl$				197.5	*c*
$[Rh(pyridine)_4Cl_2]Cl\cdot 5H_2O$				198.0	*h*
$[(dppe)Pt(AuPPh_3)_4](PF_6)_2$		686.2	136.4		*c*
$[(PPh_3)_2Pt(AuPPh_3)_3]PF_6$		686.2	136.4		*c*
NH_4PF_6		687.5	137.5		*c*
$\{(\pi\text{-}C_4H_7)Ni[P(OEt)_3]_2\}PF_6$		687.2			*i*

[a] R = 2,6-dimethylphenyl. [b] Wide peak (±0.2 eV). [c] This work. [d] Reference 27. [e] Reference 32. [f] Reference 33. [g] Reference 34. [h] Reference 35. [i] Reference 36.

Table IV. XPS Data for PF_6^- Anions[a]

compound	P 2p	F 1s	F(KVV)	α'
NH_4PF_6	137.5	687.5	600.9	1340.2
$[(PPh_3)_2Pt(AuPPh_3)_3]PF_6$	136.2	686.1	599.2	1340.5

[a] All values in electronvolts.

centered cluster compounds (average E_b = 72.2 eV). It should be noted that the effective charge of the central Pt atom in these clusters varies over a wide range and, in some cases, may not differ significantly from the charge of the peripheral Au atoms.

The ratio S_1/S_2 reported in Table I is related to the ratio of integrated intensities of the Pt 4f and Au 4f XP lines (see Results and Discussion and Figures 2 and 3 in the supplementary material[23]). A plot of the experimental S_1/S_2 values vs the Pt/Au atomic ratios for the cluster compounds (Figure 3 of supplementary material[23]) gives a straight line with a slope of 0.7, less than the theoretical value of 0.9. This deviation may be explained partly as a result of the screening effect of the peripheral gold atoms on the central Pt atom. These data and this relationship should be useful in determining the Pt/Au ratio of cluster compounds, including ones supported on surfaces.

Two of the cluster compounds investigated contain mercury. The XPS data for the Hg $4f_{7/2}$ peak are given in Table II and compared with those of metallic Hg(0) and a Hg(I) compound. According to these results, if the extraatomic relaxation energies of Hg 4f are not very different for the cluster compounds and the reference compounds, the effective charge on Hg in the cluster is less than that of Hg(I). We therefore tentatively conclude that Hg in these clusters has metallic type bonds with Au and Pt. This is consistent with the X-ray structure analyses of compound **5**[2] and $[(Hg)_2Pt(AuPPh_3)_8](NO_3)_4$.[29]

Charge of the Anions in the Cluster Compounds. Table III shows E_b data for the counteranions of the Pt–Au cluster compounds and for some noncluster compounds for comparison. There is a definite trend for the anions of the cluster compounds to have E_b's which are lower than those for noncluster compounds. For example, the NO_3^- anions of our clusters have an average N 1s E_b of 406.2 eV (range 406.0–406.3 eV) compared to 407.6 and 407.2 eV in KNO_3 and $[Hg_2(H_2O)_2](NO_3)_2$, respectively. In the case of PF_6^-, both F 1s and P 2p E_b's show the same trend (in Pt–Au clusters, 686.2 and 136.4 eV, respectively, compared with 687.5 and 137.5 eV for NH_4PF_6 and 687.2 eV for F 1s in $\{(\pi\text{-}C_4H_7)Ni[P(OEt)_3]_2\}PF_6$). This same trend is also apparent for BF_4^- and Cl^- salts (Table III). The lower E_b for the cluster anions indicates that the charge is more negative compared with the charges of anions of simple salts.

In order to further study this phenomenon, we measured the positions of F 1s and P 2p photoelectron peaks and also the F(KVV) Auger peak in the XP spectra of NH_4PF_6 and $[(PPh_3)_2Pt(AuPPh_3)_3]PF_6$. These data are presented in Table IV. The positions of the Auger peaks on the scale of binding energy correspond to 599.2 and 600.9 eV for cluster and simple salts, respectively. It is also known that the change in the modified Auger parameter α' $\{\alpha' = E_b(\text{F 1s}) + E_{kin}[\text{F(KVV)}]\}$ is proportional to extraatomic relaxation energy.[25,30] According to Mason,[25] $\Delta\alpha' = 2\Delta R_{ex}$, and from the experimental values for F 1s and F(KVV) it was found that the values for α' are equal to 1340.5 and 1340.2 eV for $[(PPh_3)_2Pt(AuPPh_3)_3]PF_6$ and NH_4PF_6, respectively. Therefore, $\Delta E_b(\text{F 1s}) \approx -\Delta\epsilon(\text{F 1s})$, where ϵ is the term for the orbital energy calculated by solving the Hartree–Fock equation by Koopmans's theorem.[31] These results permit us to conclude that for cluster compounds there is a more complete electron transfer from cation to anion than in the case of simple salts. To our knowledge, this observation has not been previously made.

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Supplementary Material Available: A discussion of the S_1/S_2 data and three figures showing the XP (C 1s) spectrum of cluster **14**, the XP spectrum of **4** in the region of the Au 4f and Pt 4f lines, and a plot of the S_1/S_2 intensity ratio for the clusters as a function of atomic Pt/Au concentration (4 pages). Ordering information is given on any current masthead page.

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