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X-ray Photoelectron Spectroscopy Study of Gold Cluster and Gold(I) Phosphine Compounds

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X-ray photoelectron spectra have been measured of the gold cluster compounds $Au_{11}L_7X_3$, $[Au_9L_8]^{3+}[Y]_3$, and $[Au_8L_8]^{2+}[Y]_2$ with L = triarylphosphine, X = Cl, I, SCN, or CN, and Y = PF_6, ClO_4, or NO_3. These were compared with XPS spectra of a series of gold(I) compounds with the same ligands. All gold atoms in the gold cluster complexes have the same binding energy for 4f electrons as in the gold(I) compounds. The Au(5d) valence band does not show any broadening attributable to d-electron delocalization. These results support the earlier conclusions drawn from Mössbauer data that there are only weak bonds between the peripheral gold atoms in the gold cluster compounds. The intensities of XPS lines were also measured and found to be consistent with the composition quoted for the various compounds and with theoretical cross sections.

Introduction

In two recent papers Vollenbroek et al.[1,2] have presented results of a Mössbauer study of two types of gold cluster compounds: $Au_{11}L_7X_3$ and $[Au_9L_8]^{3+}[Y]_3$, where L = triarylphosphine, X = Cl, I, SCN, or CN and Y = PF_6, ClO_4, or NO_3. In both types, one central gold atom has bonds with all other (peripheral) gold atoms of the cluster, which are bonded to the ligands L and X. This is illustrated in Figures 1 and 2. From the Mössbauer spectra it was concluded that the electronic structure is best described by considering the peripheral gold atoms to be linearly coordinated to the central gold atom on one side and the triarylphosphine or (pseudo-)halide on the other side. This implies that only weak bonding exists between the peripheral gold atoms. Consequently, the main difference in the electronic structure is caused by the attached ligands. This viewpoint conflicts with molecular orbital calculations by Mingos[3] and with an X-ray photoelectron spectroscopy (XPS) study by Battistoni et al.[4] The MO calculations indicated that appreciable differences in net charge exist between the various gold atoms in the cluster, and the XPS data of Battistoni et al.[4] seemed to corroborate this result as several Au 4f binding energies were found. In this paper we present results of XPS measurements of several Au_9 and Au_{11} clusters and of a new cluster compound containing eight gold atoms.[5] To aid in the interpretation, we have also measured several Au(I) compounds with the same ligands as present in the cluster compounds.

If there is appreciable bonding between peripheral gold atoms in the cluster, one expects this to have a measurable effect on the width of the gold 5d level. Calculations of the band structure of small metallic clusters of Ni and Pt indicate that already for 13 atoms the d-band width resembles that of the bulk metals.[6] We have therefore measured the 5d bands of both Au(I) and gold cluster compounds rather extensively. The large number of compounds measured has prompted us to measure the intensities of the various XPS lines as well in an attempt to assess the possibilities of XPS for quantitative analysis.

Experimental Section

A Leybold-Heraeus LHS-10 spectrometer equipped with a Mg anode was used to measure the X-ray photoelectron spectra. Lines due to X-ray satellites were removed from the measured spectra with a computer program described elsewhere.[7] Although the minimum instrumental resolution of this spectrometer is 0.64 eV, we have used a resolution of 0.8 eV throughout this study to increase the count rate.

The cluster compounds were prepared by F. A. Vollenbroek[8] and the Au(I) phosphine complexes by J. G. M. van der Linden.[8] Samples for XPS measurements were prepared by evaporation on graphite of a dilute solution of the compound in dichloromethane. It was found recently that by using graphite as a substrate, the decomposition rate of gold(III) dithiocarbamate complexes can be considerably reduced.[9] In those cases where decomposition was found to be appreciable (cluster compounds), the decomposition was further reduced by decreasing the temperature of the sample to -150 °C. The Au(4f) line was monitored repeatedly and the measuring time limited to prevent buildup of decomposition.

Although graphite has a very weak valence band intensity in XPS spectra,[10] the samples were usually so thin that the graphite background interfered with the valence bands of the compounds. The measured valence band spectra were, therefore, corrected for the graphite background by subtracting the spectrum of the graphite substrate. The scaling factor was determined from an analysis of the measured C(1s) line.

Results

A list of the Au(I) compounds that were measured is given in Table I, which presents the positions of the main XPS lines of each element present. All these compounds are nearly linearly coordinated with a triarylphosphine ligand on one side and, with a few exceptions, a (pseudo-)halide on the other side.

The determination of the binding energy of electrons in nonconducting solids presents a fundamental difficulty. In conducting solids the absolute binding energy can be determined from the photoelectron kinetic energy, only when the work function of the compound is known. Where this is mostly not the case, binding energies in conductors are usually referred to the Fermi energy. Such an internal standard is not available in nonconducting solids. This problem is confounded by the fact that due to photoemission an insulating solid can acquire a net positive charge and the resulting potential difference with the spectrometer housing sometimes leads to very large shifts (several electron volts) in the measured kinetic energy of the photoelectrons. In our case all compounds contain phosphorus in a di- or triarylphosphine ligand, and we have chosen the P(2p) line of this phosphorus atom as the internal standard. The popular choice of an aryl or alkyl C(1s) as a standard was not used because of overlap with the C(1s) of the graphite substrate. The P(2p) kinetic energy was set at 1117.0 eV. The

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Table I. Kinetic Energies of the Core Levels in the Gold(I) Phosphine Compounds Corrected for Differences in Charging with $P(2p) = 1117.0$ eV^a

compd	Au(4f$_{7/2}$)	P(2s)	Cl(2p$_{3/2}$)^c	Cl(2p$_{3/2}$)^d	Br(3p$_{3/2}$)	Br(3d)	I(3d$_{5/2}$)	I(4d$_{5/2}$)	S(2p)	N(1s)	O(1s)
AuLCl^b	1163.5	1059.7		1050.1							
AuL'Cl	1163.3	1059.5	1048.2	1050.5							
AuLBr	1163.4	1059.5			1066.7	1180.1					
AuL'Br	1163.5	1059.5	1048.4		1066.7	1179.8					
AuLI	1163.7	1059.5					629.1	1198.8			
AuL'I	1163.8	1059.7	1048.2					1198.7			
AuL'CN	1163.2	1059.5	1048.4							850.3	
AuL'SCN	1163.4	1059.5	1048.6						1086.0	850.2	
Au$_2$(DPM)Cl$_2$	1163.4	1059.3		1050.5							
Au$_2$(DPE)Cl$_2$	1163.5	1059.3		1050.6							
Au$_2$(DPP)Cl$_2$	1163.4	1059.5		1050.5							
AuLNO$_3$	1163.6	1059.5								849.0	716.5
AuL$_2$NO$_3$	1163.9	1059.6									717.1
Au$_2$DPM(NO$_3$)$_2$	1163.9	1059.7									716.8
AuL$_2$B(C$_6$H$_5$)$_4$	1163.6	1059.3									

^{a} The estimated uncertainty in the positions is ±0.2 eV.　^{b} L = P(C$_6$H$_5$)$_3$; L' = P(p-ClC$_6$H$_4$)$_3$; DPM = (C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$; DPE = (C$_6$H$_5$)$_2$PC$_2$H$_4$P(C$_6$H$_5$)$_2$; DPP = (C$_6$H$_5$)$_2$P-n-C$_3$H$_6$P(C$_6$H$_5$)$_2$.　^{c} Chlorine substituted in the benzene ring.　^{d} Chlorine directly bound to gold.
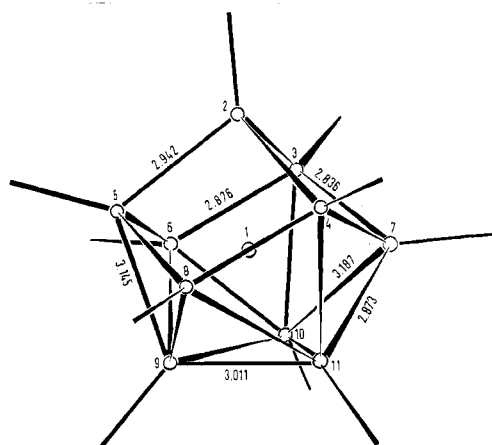
Figure 1. Structure of gold cluster in Au$_{11}$[P(p-FC$_6$H$_4$)$_3$]$_7$I$_3$. Sites 6, 7, and 8 are coordinated to iodine and the others to P(p-FC$_6$H$_4$)$_3$.
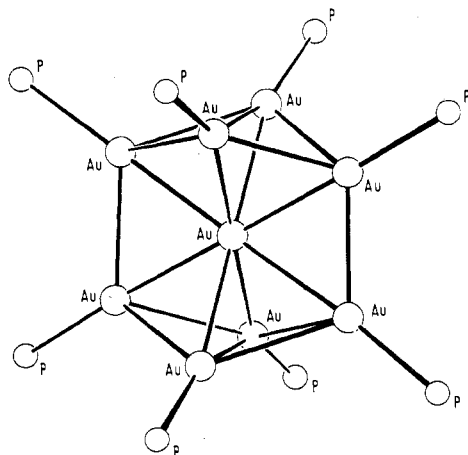
Figure 2. Au–P skeleton in Au$_9$[P(C$_6$H$_5$)$_3$]$_8^{3+}$.

Table II. Ratios of the Area Intensities per Atom in the Au(I) Compounds^d

compd	Au(4f)/ P(2p)	P(2s)/ P(2p)	Cl(2p)/ P(2p)	Au(4f)/ Cl(2p)
AuLCl^a	13.8	0.65	1.70	8.1
AuL'Cl	11.3	0.70	1.56	7.2
AuLBr	12.9	0.63		
AuL'Br	13.7	0.74	1.72	8.0
AuLI	14.7	b		
AuL'I	14.2	b	1.89	7.5
AuL'SCN	17.2	0.70	2.10	8.2
Au$_2$(DPM)Cl	15.9	0.70	1.98	8.1
Au$_2$(DPE)Cl	12.1	0.71	1.59	7.6
Au$_2$(DPP)Cl	15.2	0.68	1.86	8.1
av	14 ± 2	0.67 ± 0.1	1.8 ± 0.2	7.8 ± 0.3
calcd^c	13.7	0.83	1.95	7.0

^{a} L = P(C$_6$H$_5$)$_3$; L' = P(p-ClC$_6$H$_4$)$_3$; DPM = (C$_6$H$_5$)$_2$PCH$_2$P-(C$_6$H$_5$)$_2$; DPE = (C$_6$H$_5$)$_2$PC$_2$H$_4$P(C$_6$H$_5$)$_2$; DPP = (C$_6$H$_5$)$_2$P-n-C$_3$H$_6$P(C$_6$H$_5$)$_2$.　^{b} Not determined due to overlap of P(2s) and I(4s).　^{c} From eq 1.　^{d} The estimated errors in the ratios are 10%.

kinetic energy values can be compared with binding energy values relative to the C(1s) line at a binding energy of 285.0 eV[11] with the relation $E_{kin} = 1249.15 - E_B$, where E_{kin} and E_B are the kinetic energy of the photoelectron and the binding energy, respectively, and the value of 1249.15 is the kinetic energy of an electron ejected from the Fermi level.

In Table II we list the experimental ratios of the area intensities per atom of the Au, P, and Cl in the Au(I) compounds. The values obtained on the different compounds agree within 10–15%. For the geometry in our equipment the intensities per atom are given by[12]

$$\frac{I_1'}{I_2'} = \frac{I_1/N_1}{I_2/N_2} = \frac{\sigma_1(\epsilon_1)}{\sigma_2(\epsilon_2)} \frac{[1 + \beta_1(\epsilon_1)/16]}{[1 + \beta_2(\epsilon_2)/16]} \frac{T(\epsilon_1)}{T(\epsilon_2)} \frac{\lambda(\epsilon_1)}{\lambda(\epsilon_2)} \quad (1)$$

where $\sigma_i(\epsilon_i)$ is the cross section for photoionization from level i, $\beta_i(\epsilon_i)$ is the angular anisotropy parameter, $T(\epsilon_i)$ is the transmission of the spectrometer at energy ϵ_i, and $\gamma(\epsilon_i)$ is the mean free path in the sample under consideration of an electron with energy ϵ_i. The theoretical values of the cross sections for photoionization with Mg K$\alpha_{1,2}$ radiation have been calculated by Scofield.[13] The anisotropy parameters $\beta_i(\epsilon_i)$ are given by Reilman et al.[14] Because of the geometry, the angular anisotropy parameter $\beta(\epsilon)$ has only a minor effect on the relative intensity. The transmission of the LHS-10 electron spectrometer is inversely proportional to the kinetic energy of the electron.[15] Penn[16] has presented calculations of the mean free path for pure elements and for compounds, but his results deviate strongly from experimental data on KI.[17] We use the

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Table III. Kinetic Energies, Corrected for Differences in Charging with P(2p) of the Triarylphosphine Group Set Equal to 1117.0 eV, of the Core Levels in the Gold Cluster Compounds[g]

compd	Au(4f$_{7/2}$)	P(2s)[b]	P(2s)[c]	P(2p)[c]	Cl(2p$_{3/2}$)[d]	Cl(2p$_{3/2}$)[e]	F(1s)	S(2p)	N(1s)	O(1s)
Au$_9$L$_8$(ClO$_4$)$_3$[a]	1163.2	1059.3				1041.2				716.1
Au$_9$L$_8$(PF$_6$)$_3$	1163.4	1059.3	1055.4	1112.3			562.3			
Au$_9$L$_8$(NO$_3$)$_3$[f]	1163.9	1059.5								716.2
Au$_{11}$L$_7$(SCN)$_3$	1163.7	1059.4						1085.8	850.6	
Au$_{11}$L'$_7$(SCN)$_3$	1163.5	1059.5			1048.2			1085.8		
Au$_8$L$_8$(PF$_6$)$_2$	1163.5	1059.4	1055.3	1112.4			562.6			

[a] L = P(C$_6$H$_5$)$_3$; L' = P(p-ClC$_6$H$_4$)$_3$. [b] Phosphorus of the triarylphosphine group. [c] Phosphorus of the PF$_6$ group. [d] Chlorine substituted in the benzene ring. [e] Chlorine of the ClO$_4$ group. [f] Measured at room temperature. [g] The estimated uncertainty in the positions is ±0.2 eV. The measurements were done at −150 °C.

Table IV. Ratios of the Area Intensities per Atom in the Gold Cluster Compounds[c]

compd	Au(4f)/P(2p)	P(2s)/P(2p)	Cl(2p)/P(2p)	Au(4f)/Cl(2p)	PF$_6$/P(C$_6$H$_5$)$_3$[b]
Au$_9$L$_8$(ClO$_4$)$_3$[a]	15.3	0.74	1.5	9.5	
Au$_9$L$_8$(PF$_6$)$_3$	13.0	0.66			0.37 [0.38]
Au$_9$L$_8$(NO$_3$)$_3$	16.8	0.72			
Au$_{11}$L$_7$(SCN)$_3$	13.5	0.67			
Au$_{11}$L'$_7$(SCN)$_3$	13.9	0.65	2.1	6.7	
Au$_8$L$_8$(PF$_6$)$_2$	14.3	0.74			0.25 [0.25]

[a] L = P(C$_6$H$_5$)$_3$; L' = P(p-ClC$_6$H$_4$)$_3$. [b] Experimental ratio of the phosphorus lines of the PF$_6$ group and the P(C$_6$H$_5$)$_3$ group. The values in brackets are the theoretical values. [c] The estimated errors in the ratios are 10%.
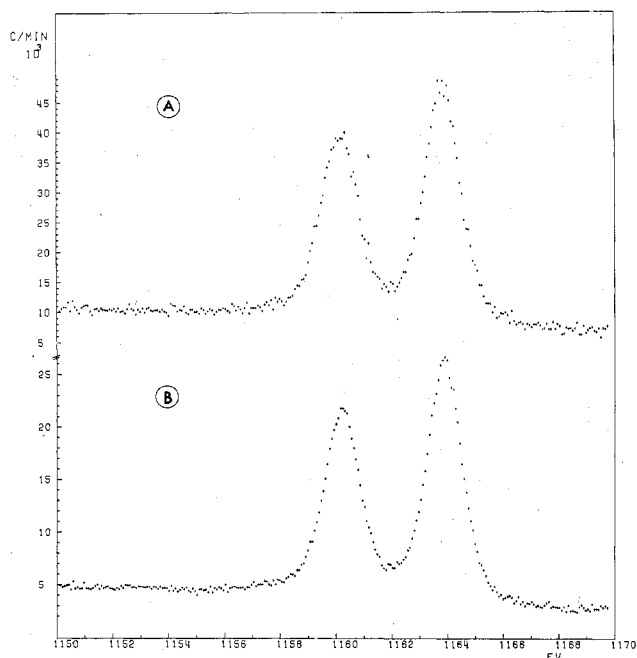

Figure 3. X-ray photoelectron spectrum of the Au(4f) levels in AuP(p-ClC$_6$H$_4$)$_3$Br (A) and Au$_9$[P(C$_6$H$_5$)$_3$]$_8$[ClO$_4$]$_3$ (B). The spectra have been corrected for the X-ray satellites, but no correction for the charging was made.

approximate expression λ(ϵ_i) = α(ϵ_i)$^{1/2}$ where α is a constant. The theoretical values for I_1'/I_2' calculated with eq 1 are also given in Table II. The agreement between calculated and experimental values is good, except for the P(2s)/P(2p) ratio. In view of the general agreement between experimental and theoretical values, it is probable that the calculated value of the P(2s) cross section is too large.

Table III lists the positions of the main XPS lines of the cluster compounds that have been investigated. The Au$_8$[P-(C$_6$H$_5$)$_3$]$_8$[PF$_6$]$_2$ complex is a new cluster compound reported

(17) J. Szajman, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, *Phys. Rev. B*, **18**, 4010 (1978).

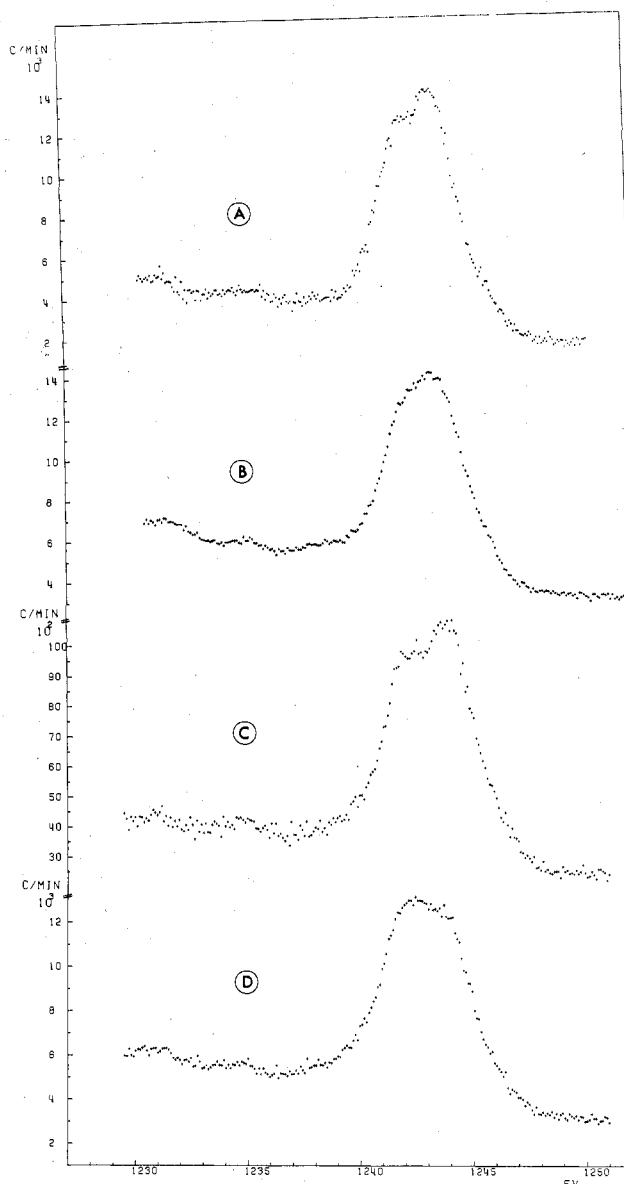**Figure 4.** X-ray photoelectron spectra—after correction for the substrate valence band—of the valence bands in AuLSCN (A), AuL'SCN (B), Au$_{11}$L$_7$(SCN)$_3$ (C) and Au$_{11}$L'$_7$(SCN)$_3$ (D) where L = P(C$_6$H$_5$)$_3$ and L' = P(p-ClC$_6$H$_4$)$_3$. The spectra are normalized on the Au(4f$_{7/2}$) line.

recently by Vollenbroek et al.[5] The geometry of the Au$_8$ skeleton can be described as being derived from that of the Au$_{11}$ cluster given in Figure 1 by removal of the three gold atoms in the basal triangle. Only one Au 4f doublet was observed in all cluster compounds. Figure 3 illustrates the close similarity between the Au(4f) spectrum of a gold(I) phosphine complex and a cluster compound. The observed line width

is in both cases 1.5 ± 0.1 eV. This is larger than that measured for gold metal (1.2 eV) at the same spectrometer resolution and is probably due to small inhomogeneities in the charging of the sample. Table IV gives the experimental ratios of the area intensity per atom of the Au, P, and Cl in the gold cluster compounds. There is excellent agreement with the values found for the gold(I) phosphine complexes.

In Figure 4 are shown the valence bands of AuLSCN, AuL'SCN, $Au_{11}L_7(SCN)_3$, and $Au_{11}L'_7(SCN)_3$ where L = $P(C_6H_5)_3$ and L' = $P(p\text{-}ClC_6H_4)_3$. As in the case of the binding energies a close similarity is found for the gold(I) phosphine compounds and the gold cluster complexes.

Discussion

$AuP(C_6H_5)_3Cl$ and $Au_2(C_6H_5)_2P(CH_2)P(C_6H_5)_2Cl_2$ have been measured by van de Vondel et al.,[11] and there is excellent agreement with the present results. Battistoni et al.[4] studied a series of mononuclear gold compounds. After correction for the different internal standards there is good agreement between their values and those reported here. For the gold(I) compounds studied by us there is surprisingly little variation in the kinetic energy of the Au(4f) lines, but there is significant difference with the kinetic energy of the Au(4f) lines reported elsewhere[9] for gold(I) dithiocarbamates (Au(dtc)), where gold is coordinated to two sulfur atoms. The kinetic energy of the Au(4f) lines of the $Au^I(dtc)$ complexes is 1.0 eV larger. A similar difference was found by van de Vondel et al.[11] between $AuP(C_6H_5)_3Cl$ and $Au_2(S_2P(C_2H_5)_2)_2$, which also contains two sulfur atoms directly connected with Au(I).

The cross section ratios per atom for the gold(I) phosphine complexes agree with each other within 10–15%. The corresponding ratios for the gold cluster compounds lie within the same range; i.e., they are in agreement with the quoted nominal compositions of the gold cluster compounds.

The binding energies of the Au(4f) electrons in the gold cluster compounds are identical with those of the gold(I) phosphine complexes. It is surprising, that in the 4f spectra no trace is found of the central gold atom, for which one expects an electronic structure different from the peripheral gold atoms. Apparently, the Au(4f) binding energy of the central gold atom is very close to that of the peripheral gold atoms. In view of the widths of the 4f lines and the small relative intensity of the line due to the central gold atom, we estimate the maximum binding energy difference to be less than 0.5 eV. This result may be a consequence of equalization of potential at the central gold atom due to a Madelung po-

tential opposing the difference in charge. Also, the difference in charge between the central gold atom and the peripheral gold atoms may be very small in spite of the difference in electronic configuration. Battistoni et al.[4] observed the appearance of extra 4f lines in the XPS spectra of the cluster compounds. These additional lines, however, must be ascribed to decomposition products, since we observe these lines only after prolongated measuring times.

The valence band of both the gold(I) phosphine compounds and gold cluster complexes consists, generally, of a doublet due to the spin–orbit split Au(5d) bands and a shoulder the intensity of which depends on the ligands. The 5d bands of the cluster compounds do not show any broadening compared to those of the gold(I) phosphine complexes. This indicates that no significant d-electron delocalization occurs in the gold clusters. The spin–orbit splitting is 1.6 ± 0.2 eV. When $P(p\text{-}ClC_6H_4)_3$ is present, the splitting of the 5d lines is no longer resolved: the Cl(3p) line of this ligand is situated between the two 5d bands. Subtracting the normalized valence band spectrum of $Au_pL_qX_r$ from that of $Au_pL'_qX_r$ (L = $P(C_6H_5)_3$ and L' = $P(p\text{-}ClC_6H_4)_3$) we found a single line at 1242.3 ± 0.3 eV. The energy difference with the corresponding Cl($2p_{3/2}$) line is 193.9 ± 0.4 eV, in good agreement with a separation of 193.2 eV that we found in KCl.

A number of other results are noteworthy: The kinetic energy of the Cl($2p_{3/2}$) line of the chlorine directly bound to gold is 2.1 ± 0.2 eV higher than that of the chlorine in the benzene rings. For the phosphorus atoms in PF_6 and $P(C_6H_5)_3$, a difference of 4.5 ± 0.2 eV is found, in good agreement with literature.[18]

In conclusion, there is a close similarity between the XPS of gold(I) phosphine compounds and of the gold cluster complexes, including the Au(5d) bands. This result supports the description of the peripheral gold atoms as being linearly hybridized.

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