in accord with the computational result, but the general picture is reasonable. Once again, a high degree of mixing of the dπ and dδ orbitals is revealed by the quantitative treatment. It is not, of course, surprising that since this occurred in $[Ru_2Cl_9]^{3-}$ it would continue to occur in the homologous $[Ru_3Cl_{12}]^{4-}$ ion.

The Ru–Ru distances in the $[Ru_2Cl_9]^{3-}$ and $[Ru_3Cl_{12}]^{4-}$ ions, 2.725 (3) and 2.805 (1) Å, respectively, are consistent with the formal bond orders of 1.0 and 0.5, respectively. Obviously, in structures of this kind where the metal–metal distance is a function of several other factors, especially the presence of bridging atoms, no simple quantitative correlation between metal–metal distance and metal–metal bond order alone is to be expected.

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Photoelectron Spectra and Bonding in Some Trimethylgold(III) Complexes

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The He I and He II photoelectron spectra of three Au(III) complexes, $[AuMe_3L]$ (L = PMe_3, PMe_2Ph, and $PMePh_2$), have been recorded in the gas phase. The spectra have been assigned with use of the previously assigned $[AuMe(PMe_3)]$ spectrum and the cross section differences between the He I and He II spectra. The Au $5d_{x^2-y^2}$ orbital is heavily involved in bonding—mainly to the phosphines. An attempt is made to assign the other Au 5d ionizations in a rather small (0.75 eV) range. Trends in binding energies for the three complexes indicate that the donor strength of the phosphines increases in the order $PMe_3 < PMe_2Ph < PPh_2Me$. A semiquantitative molecular orbital diagram for these complexes is constructed.

Introduction

Organogold(III) complexes, $[AuMe_3L]$ (L = phosphine), are found to undergo reductive elimination of ethane after dissociation of the phosphine ligand. Their catalytic properties in providing a pathway for the coupling between alkyllithium reagents and alkyl halides are well recognized.[1-3] The thermal stability of $[AuMe_3L]$ thus depends on the ease of dissociation of L, giving rise to gold(III) ($AuMe_3$) and gold(I) ($AuMe$) species as reactive intermediates. The presence of a strong Au–L bond, which is not readily cleaved, is responsible for the thermal stability of these complexes.[4]

As a continuation of our study of the bonding in gold phosphine complexes,[5,6] we report the He I and He II photoelectron spectra of three square-planar[7] $[AuMe_3L]$ (L = PMe_3, PMe_2Ph, $PMePh_2$) complexes. We had two major objectives in mind. First, we wanted to clarify the order of σ-donor ability of these ligands. The better σ-donor ligand is expected to increase the electron density at the metal, leading to a smaller binding energy for the Au 5d orbitals and the Au–C σ-bonding orbital.[8] It is also expected that the phos-

phine lone-pair orbital on the best donor will be stabilized the most upon complexation. Second, the overall molecular orbital diagram and in particular the role of the Au 5d orbitals in bonding are of considerable interest.[9] In our previous photoelectron study on $[AuMe(PMe_3)]$,[5] we confirmed that the Au $5d_{z^2}$ orbital is involved in bonding; such d involvement has been widely used to explain the high tendency of Au(I) to form linear complexes.[10-12] Using our assignment of the photoelectron spectra, we are able to comment on the Au 5d involvement in bonding and derive a semiquantitative molecular orbital diagram for our Au(III) complexes.

Experimental Section

The four gold(III) complexes, $[AuMe_3L]$ (L = PMe_3, $PPhMe_2$, PPh_2Me, and PPh_3), were prepared by using literature methods.[13-15] The complexes were then characterized with use of their characteristic melting points and ^1H NMR spectra.

The He I and He II photoelectron spectra of the complexes were run on our McPherson ESCA-36 photoelectron spectrometer using a hollow-cathode ultraviolet He lamp[16] and computer fitted to Lor-

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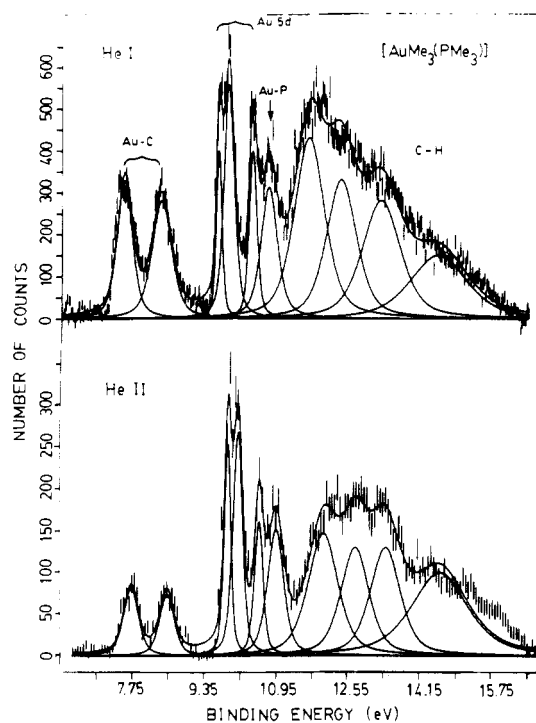
Figure 1. He I and He II photoelectron spectra of [AuMe$_3$(PMe$_3$)].

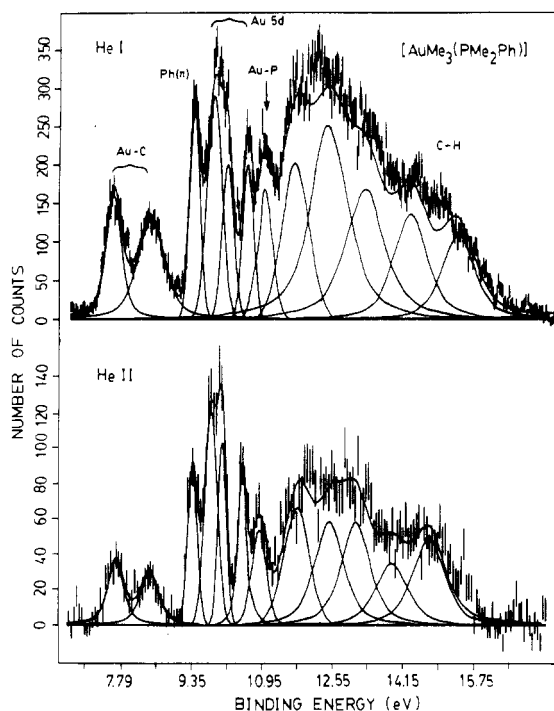**Figure 2.** He I and He II photoelectron spectra of [AuMe$_3$(PMe$_2$Ph)].

entzian–Gaussian line shapes.[17] The heated inlet system and experimental details have been outlined in previous papers.[5,18,19] The compounds had to be heated only slightly to obtain spectra. All spectra were run at high resolution ($\simeq$30 meV for He I and He II spectra), and the best count rates in the present study were ~100 counts/s with He I radiation and ~20 counts/s with He II radiation. The photoelectron spectra of [AuMe$_3$(PPh$_3$)] could not be obtained because of sample decomposition. All the spectra were calibrated with the Ar 3P$_{3/2}$ line at 15.759 eV. Ar was introduced through the sample

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Table I. Photoelectron Parameters for the He I and He II Spectra of the Three [AuMe$_3$L] Complexes and [AuMe(PMe$_3$)]

| | [AuMe(PMe$_3$)][b] | | | | [AuMe$_3$(PMe$_3$)] | | | | [AuMe$_3$(PPhMe$_2$)] | | | | [AuMe$_3$(PPh$_2$Me)] | | | |
| | | | area[c] | | | | area[c] | | | | area[c] | | | | area[c] | |
orbital	binding energy,[a] eV	fwhm, eV	He I	He II	binding energy, eV	fwhm, eV	He I	He II	binding energy, eV	fwhm, eV	He I	He II	binding energy, eV	fwhm, eV	He I	He II
Au-C	8.24	0.56	0.6	0.4	7.76	0.41	1.1	1.2	7.68	0.42	0.58	0.73	7.61	0.42	0.55	0.55
Ph π					8.59	0.51	1.3	1.0	8.49	0.69	0.82	0.71	8.31	0.58	0.72	0.51
Au 5d	9.84	0.38	1.0	1.72	9.87	0.21	1.0	1.72	9.45	0.28	0.62	0.99	9.32	0.48	1.38	2.43
Au 5d	10.55	0.36	0.8	0.6	10.10	0.21	1.2	2.0	9.88	0.38	1.00	1.72	9.73	0.43	1.00	1.72
Au 5d	11.33	0.30	0.6	1.0	10.63	0.21	0.3	1.3	10.18	0.27	0.49	1.05	10.06	0.35	0.72	0.76
Au–P	9.22	0.28	0.5	0.3	10.99	0.44	1.6	2.4	10.57	0.27	0.50	0.85	10.50	0.30	0.51	0.78
									10.95	0.4	0.72	0.92	10.92	0.45	0.90	1.03
P-C	12.00	0.7	1.7	0.5	11.89	0.8	4.2	4.4	11.63	0.7			11.59	0.70	2.07	2.36
Au–P stabilization energy, eV	0.66				2.35				2.63				2.64			

[a] The He I and He II binding energies agree to within 0.04 eV. All spectra are calibrated relative to Ar 3p$_{3/2}$ at 15.75 eV. [b] Results from ref 5. [c] Experimental intensities are divided by the peak kinetic energy and normalized to the low binding energy Au 5d peak.
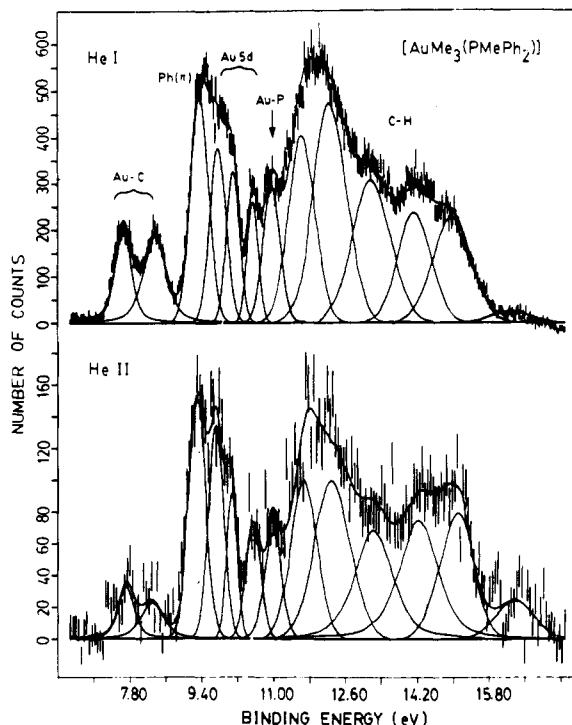
Figure 3. He I and He II photoelectron spectra of [AuMe$_3$(PMePh$_2$)].

probe via an external valve simultaneously with the sample.

Results and Discussion

The He I and He II photoelectron spectra of the three Au(III) complexes are shown in Figures 1–3. The binding energies, widths, and relative areas of the first seven (L = PMe$_3$) or eight (L = PPhMe$_2$, PPh$_2$Me) peaks of major interest are given in Table I along with the corresponding parameters for the Au(I) complex [AuMe(PMe$_3$)] studied previously.[5] The binding energies for the peaks between >12 and 17 eV are not thought to be particularly significant and are not quoted in the table. In this C–H ionization region, the same number of peaks of similar width have been fitted to simulate both He I and He II spectra of one compound in a consistent manner.

The assignment of the seven low binding peaks in the Au(III) complex [AuMe$_3$(PMe$_3$)] is greatly facilitated by our previously published spectrum of the Au(I) analogue [AuMe(PMe$_3$)][5] and the relative intensity changes from He I to He II spectra. It is well-known that the 5d cross sections increase substantially, while p cross sections decrease substantially, from He I to He II spectra (references in ref 5). In our previous paper, we set the Au $5d_{5/2}$ cross section to the atomic Hg $5d_{5/2}$ values of 1.0 and 1.72 for He I and He II spectra, respectively. For our Au(III) compounds, we set the first Au 5d peak areas at these same values to facilitate comparison of the peak areas.

The first two broad peaks at 7.76 and 8.59 eV of similar intensity are at a binding energy similar to that of the Au–C molecular orbital in the Au(I) complex, and these two peaks can be readily assigned to the symmetry-split Au–C ionization.[8] The large line widths are consistent with metal–carbon ionizations, and the intensities of these two peaks both decrease considerably *relatively* on going from He I to He II spectra, as in the Au(I) complex[5] and other organometallic compounds.[20] However, as shown in Table I, when they are corrected for the increase in the Au 5d cross section, these Au–C cross sections stay about constant from He I to He II, indicative of some Au 5d character in the Au–C bonds. The

rather similar areas of these two peaks do not help in the specific assignment of these two peaks, but it seems likely that the ionization of the two Au–C bonds cis to the incoming phosphine gives rise to the lower binding energy peak (A), while the higher binding energy peak (B) arises from the Au–C bond trans to the phosphine. The Au–C bonds cis to the phosphine have a longer bond length than the trans Au–C bond length,[7] and the lower ionization energy for peak A compared to the Au–C binding energy in the Au(I) analogue can be attributed to the presence of two mutually trans Me groups destabilizing each other in [AuMe$_3$(PMe$_3$)].[9]

We turn next to the broad peak at 11.89 eV, because this assignment is readily made to the P–C bonding orbital. As expected, this orbital has a binding energy and width very similar to the those of P–C orbital in the Au(I) analogue.

The peaks at 9.87, 10.10, 10.63, and 10.99 eV are in the same region as the Au 5d peak in the Au(I) analogue and are thus assigned to the Au 5d ionizations and the Au–P orbital. All of these peaks increase substantially in intensity *relative* to the Au–C peaks on going from He I to He II spectra. Regardless of which of these four peaks is assigned to the Au–P orbital, this intensity increase implies that the Au–P orbital has a large Au 5d character. This is consistent with the Xα–SW results on the Au(I) analogue,[5] which showed that the Au–P bond contained substantially more Au 5d character than the Au–C bond. Because of stabilization of the Au $5d_{x^2-y^2}$ orbital[21] due to bonding, we would expect the Au–P orbital to be at higher binding energy than the other Au 5d orbitals. We thus assign the peak at 10.99 eV to the Au–P orbital and the three lower binding energy peaks to the other Au 5d ionizations. Two pieces of spectroscopic evidence support this assignment. First, the intensity of this peak increases less from He I to He II spectra than the other three peaks, as expected for an orbital having some P lone-pair character. Second, this peak is considerably broader than the other three peaks, as expected for a strongly bonding orbital.

The remaining three Au 5d peaks are separated by ~0.75 eV and cannot be assigned unambiguously. We suggest two possible assignments. The first assignment, d_{z^2} (9.87 eV), d_{xz} and d_{yz} (10.10 eV), and d_{xy} (10.63 eV), is consistent with previous molecular orbital calculations on isoelectronic Pt^{2+} compounds.[22,23] However, it seems very likely that d_{xz} and d_{yz}, having very similar energies, would lead to a spin–orbit doublet and this leads to our second assignment. The spin–orbit splitting will be significantly smaller[19,24] than the free-ion value of 1.50 eV.[25] The peak at 9.87 eV would then be an overlap of the d_{z^2} peak along with one spin–orbit component of d_{xz} and d_{yz}. The other spin–orbit component would be at 10.63 eV, while the 10.10-eV peak is assigned to d_{xy}. These two assignments would lead to expected intensity patterns of 1:2:1 and 2:1:1, respectively, on the basis of the simplest degeneracy arguments. The latter assignment is a closer fit to the experimental data—especially for the other two Au(III) complexes (Table I).

The assignment of the spectra of the PPhMe$_2$ and PPh$_2$Me Au(III) complexes (Figures 2 and 3) can now be made readily. The one additional peak in these spectra at ~9.4 eV is assigned to the phenyl π orbital. It is reasonable that these orbital energies do not vary greatly from the ligand-only values of 9.17 eV (9.51-eV shoulder) and 9.19 eV (9.53-eV shoulder), respectively.[6] This assignment is further confirmed by the ap-

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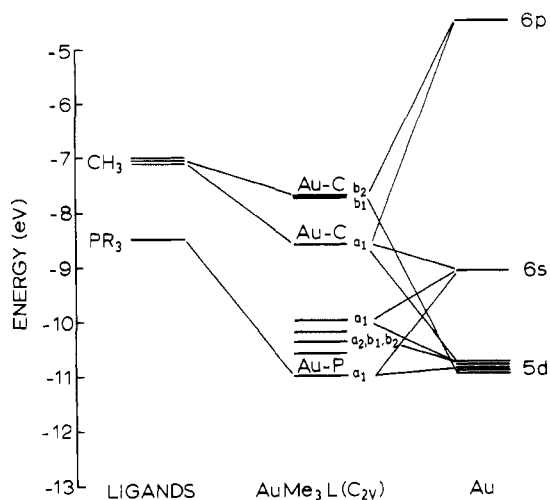(25) C. E. Moore, *Natl. Bur. Stand. (U.S.), Circ.*, No. **467** (1958).

Figure 4. Semiquantitative molecular orbital diagram for the occupied orbitals of the [AuMe₃L] complex.

proximate doubling in relative intensity of this peak from the [AuMe₃(PPhMe₂)] spectrum to the [AuMe₃(PPh₂Me)] spectrum (Table I). We do not resolve the shoulders seen in the ligand-only spectra due to the strong overlap of these Ph peaks with the low-energy Au 5d peak.

The remainder of these spectra in the 7–12-eV binding energy range are very similar to the spectra of the PMe₃ Au(III) analogue, and the assignments are identical. The Au–P peak is again the broadest of the four peaks in the Au 5d region, and the relative intensity of this peak once again increases substantially from He I to He II spectra.

Several binding energy trends are apparent in Table I. First, the binding energies of the Au–C bonding orbitals decrease substantially in the order [AuMe₃(PMe₃)] > [AuMe₃-(PMe₂Ph)] > [AuMe₃(PMePh₂)]. Second, the Au 5d and Au–P binding energies generally decrease in the same order. Third, the stabilization energy of the Au–P orbital (the difference in binding energy between the Au–P orbital in the complex and the P lone-pair orbital in the free phosphine[6]) *increases* in the same order. The above trends can be readily interpreted if the σ-donor strength of the phosphine ligands *increases* in the order PMe₃ < PMe₂Ph < PMePh₂. This order of donor strengths was initially suggested by Puddephatt and co-workers[8] and also found recently from proton affinity measurements on these phosphines.[26] It is apparent that the

mixed phenylphosphines are more effective in increasing electron density on gold than PMe₃.

We have constructed a semiquantitative molecular orbital diagram for these complexes in Figure 4. The Au atom energies are obtained from the atomic spectroscopy values,[25] and the phosphine lone-pair ionization potential is taken from the free phosphine IP from photoelectron measurements.[5,6] The methyl position is arbitrarily set at smaller energy than the phosphine, as methyl is known to be a better donor ligand. Also, this relative ordering is consistent with the relatively small Au 5d character in the Au–C bonds. The energies of the molecular orbitals of the Au(III) complex are taken from our photoelectron results (Table I). We do not specify the order of the a₂, b₁, and b₂ d orbitals because our assignment is only tentative in this region. The majority character of the MO's is indicated by the lines from the ligand and Au orbitals. Thus, the Au–C orbitals have significant Au 5d character as well as Au 6s and Au 6p character, while the Au–P bond probably has mainly Au 5d and Au 6s character with little Au 6p character.

Our molecular orbital diagram agrees qualitatively but differs quantitatively from those calculated by Hoffmann et al.[9,27] for Me–Au fragments. Our molecular orbital energies are all somewhat smaller, and the range of energies is much smaller, mainly because the Au 5d energies were calculated at ∼15 eV[9,27] rather than the ∼11 eV from atomic values. Since the Hg 5d energies are very similar in atomic Hg and Me₂Hg[20,28] (within 0.2 eV), it is reasonable that the Au 5d energies in our Au(I) and Au(III) complexes will also be at energies very similar to the atomic Au values. Also, since the Hg 5d, Tl 5d, and Pb 5d energies are ∼15,[28] ∼21,[29] and ∼26 eV,[30] it is not reasonable that the Au 5d energies would lie at ∼15 eV.

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