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Assignment of the Valence Molecular Orbitals of $CpPtMe_3$ and $Me_2Pt(COD)$ Using Variable-Energy Photoelectron Spectra

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High-resolution variable-energy photoelectron spectra are reported for the upper valence band region of $CpPtMe_3$ ($Cp = \eta^5\text{-}C_5H_5$) and $Me_2Pt(COD)$ (COD = 1,5-cyclooctadiene) for photon energies between 21 and 100 eV. $X\alpha$–SW results on the $CpPtMe_3$ valence levels are also reported as the basis for the spectral assignment. Experimental and theoretical branching ratios are in good agreement with the $X\alpha$–SW assignment but are inconsistent with the previous Fenske–Hall assignment for the $CpPtMe_3$ valence ionizations. Contrary to the Fenske–Hall assignment, our present results strongly indicate that the nonbonding Pt 5d orbitals are not the HOMO's and have higher ionization potentials than several Pt–L orbitals. Comparisons of the observed and calculated branching ratios also confirm a previous $X\alpha$–SW assignment for the $Me_2Pt(COD)$ valence ionizations. Intensity changes of the ionization bands for the two molecules as a function of photon energy are largely dependent on the relative values of the Pt 5d and C 2p atomic cross sections (the Gelius model). There are no obvious resonance enhancements of any of the cross sections.

Introduction

In the interpretation of organometallic photoelectron spectra taken with conventional He I and He II ionization sources, an empirical intensity rule is often used to distinguish metal d-based orbital ionizations from ligand p-based orbital ionizations. This intensity rule states that a metal d-based orbital ionization generally shows an intensity increase from He I ($h\nu = 21.22$ eV) to He II ($h\nu = 40.81$ eV) ionization sources, compared to a ligand p-based orbital ionization.[1,2] The empirical rule is based on the fact that metal d cross sections increase, while ligand p cross sections decrease from He I to He II photon energies. It is then assumed that molecular orbital cross sections can be determined by summation of the constituent atomic cross sections and that contributions from the orbital overlap interactions can be neglected. This assumption is known as the Gelius model.[1] Often this intensity rule has been successful in interpreting the valence photoionization spectra of organometallics.[2] However it has also been challenged by inconsistent observations between ionization energy shifts and intensity variations and by theoretical predictions. A well-known example is given by the valence spectrum of $Ni(C_3H_5)_2$, for which numerous experimental and theoretical studies have failed to yield a definitive assignment.[3]

In our photoelectron studies of Pt compounds, it has been observed that dimethylplatinum(II) and trimethylplatinum(IV) compounds did not show pronounced He II/He I intensity ratio differences between the Pt 5d and ligand p-based orbital ionizations, so that the intensity rule could not be used to assign the spectra.[4] The small intensity changes probably result largely from the small Pt 5d atomic cross section differences at He I and He II energies (29.46 Mb at 21.2 eV and 31.3 Mb at 40.8 eV)[5] and from the heavy mixing of the Pt and ligand orbitals in these covalent organometallic compounds. Therefore, the interpretation of the photoionization bands was largely based on theoretical predictions and other experimental evidence, such as vibrational splittings and energy shifts.[4] For $CpPtMe_3$ ($Cp = \eta^5\text{-}C_5H_5$), the assignment was based largely on Fenske–Hall calculations,[4b] which gave the ionization energy ordering Pt $5d_\pi$ < Pt–Me < Pt–Cp with the Pt $5d_\pi$ orbitals being the HOMO's. However, in our subsequent photoelectron studies of both Pt(II) and Pt(IV) compounds,[4] $X\alpha$–SW calculations and spectroscopic evidence always indicated that the Pt 5d orbitals had ionization energies higher than several Pt–L orbitals. These results therefore cast doubt on the Fenske–Hall assignment for $CpPtMe_3$.

In this paper, we use a three-pronged approach to confirm the valence orbital ordering of $CpPtMe_3$[4b] and a Pt(II) compound $Me_2Pt(COD)$ (COD = 1,5-cyclooctadiene).[4a,c] First, an $X\alpha$–SW calculation was carried out for $CpPtMe_3$,[6] to see whether the valence level assignment agreed with the Fenske–Hall ordering or the ordering anticipated from our $X\alpha$–SW calculations on the other Pt(II) and Pt(IV) compounds.[4c,d] Second, and most importantly, we have used monochromatized synchrotron radiation to obtain relative valence orbital cross sections (branching ratios) from variable-energy photoelectron spectra between 21- and 100-eV photon energies. Combined with theoretical $X\alpha$–SW cross section calculations, such spectra have proven to be invaluable for resolving theoretical contradictions in reasonably large inorganic molecules. For example, for XeF_2, ab initio and $X\alpha$–SW calculations predicted a different ordering of the molecular orbitals, but cross sections and branching ratios from the variable-energy photoelectron spectra were only consistent with the $X\alpha$–SW assignment.[7] Third, as a further confirmation of the assignment, we have compared our experimental branching ratios with those obtained from the Gelius model from the Fenske–Hall and $X\alpha$–SW assignments.

Experimental Methods

Preparation and purification of $CpPtMe_3$ and $Me_2Pt(COD)$ were described previously.[4b,c]

Gas-phase photoelectron spectra were obtained at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin—Madison.[8] A 900 groove/mm grating at photon energies >40 eV and a 600 groove/mm grating at photon energies <40 eV were used in the *Grasshopper* grazing incidence monochromator. Practical minimum photon resolutions were 0.02 eV at a photon energy of 30 eV and 0.09 eV at 80 eV with 30-μm slits. The photon beam emerging from the monochromator exit slit was refocused to the gas cell in the new photoelectron chamber.[9] The resultant photoelectrons were

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analyzed with a McPherson electron analyzer, which was mounted at the pseudo magic angle, and detected with a channeltron detector, which was linked to a specially designed amplifier-discriminator and connected to a counter unit interfaced with a Zenith Z-158 PC microcomputer. This computer also controlled the spectrometer electron energy by scanning through a Biodata Microlink interface unit and the McPherson high-stability voltage power supply.[9]

The solid samples of CpPtMe$_3$ and Me$_2$Pt(COD) were introduced through a probe into the gas cell, which was heated by a resistance heater in order to achieve sufficient pressure in the gas cell ($\sim 10^{-2}$ Torr), while giving a low pressure ($\sim 4 \times 10^{-5}$ Torr) in the sample chamber. The spectra were recorded from photon energies of 21–100 eV, with energy steps of 2 eV below 55 eV and of 5 eV above 55 eV. Band areas were obtained by fitting the spectra with an iterative procedure[10] and corrected for the electron analyzer transmission energy by dividing by the kinetic energy of the band. Experimental branching ratios were obtained by using the resulting band areas (A_i) and the branching ratio definition ($\mathrm{BR}_i = A_i/\sum A_i$).

Computational Details

The upper valence orbital ionization energies and electron distributions of the molecule CpPtMe$_3$ were calculated by using the relativistic version of the Xα–SW method.[11] Geometrical data were taken from the mean values of the crystal structure as in the previous Fenske–Hall calculation,[4b] and the molecule was idealized to C_s symmetry. The exchange α parameters and sphere radii were chosen as described previously.[4c,12] An $l_{\max}$ of 3 was used for the outer-sphere region and the Pt atom, whereas $l_{\max}$ values of 1 and 0 were used for C and H atoms, respectively. For Me$_2$Pt(COD), previous Xα–SW potentials and charge distributions were used for the theoretical partial ionization cross section calculations.[4c] In the Xα–SW cross section calculations, the transition-state converged potentials of both CpPtMe$_3$ and Me$_2$Pt(COD) (corrected for asymptotic behavior with a Latter tail[13]) were used and the calculations were performed by using Davenport's program.[14] The $l_{\max}$ values for the final state were extended to 7, 5, 2, and 1 around the outer-sphere, Pt, C, and H regions, respectively. The resulting partial cross sections (σ_i) for the upper valence orbitals were first used to calculate theoretical branching ratios ($\mathrm{BR}_i = \sigma_i/\sum\sigma_i$) for each orbital at each photon energy and then combined (if necessary) according to the spectral assignments. The Xα–SW cross sections were calculated by using the Xα–SW orbital characters for each of the assignments based on the Xα–SW and the Fenske–Hall calculations. This method is clearly less satisfactory for the Fenske–Hall assignment. Therefore, Gelius model calculations were also carried out. Branching ratios ($\mathrm{BR}_i = \sigma_i/\sum\sigma_i$) based on the simple Gelius model were performed by using the formula[1,15]

$$\sigma_i \propto \sum (P_{A_j})_i \sigma_{A_j} \qquad (1)$$

assuming a magic angle between the photon beams and the emitted photoelectrons. $(P_{A_j})_i$, the "probability" of finding in the ith MO an electron belonging to an atomic orbital A_j, was approximated as the charge distribution from the Xα–SW calculations for both CpPtMe$_3$ and Me$_2$Pt(COD) and also from the Fenske–Hall calculations for CpPtMe$_3$.[4b] σ_{A_j}, the cross section of the atomic orbital A_j, is calculated from the fitted polynomial functions which were obtained by using the theoretical atomic cross section values at photon energies 16.7, 21.2, 26.8, 40.8, 80.0, and 132.3 eV.[5]

Results and Discussion

(A) CpPtMe$_3$. Photoelectron spectra of CpPtMe$_3$ at 23-, 39-, 55-, and 90-eV photon energies are presented in Figure 1. These are very similar in quality to the He I spectrum reported previously.[4b] It is immediately obvious from the spectra that bands A and B display a relative intensity reduction as the photon energy increases from 23 to 90 eV. The observations here are generally in accord with those from our conventional He I and He II spectra,[4b] but the conclusion about this reduction is now much more certain in the current work, because the intensity changes are greater over the much larger energy range studied and because there are many more observations.

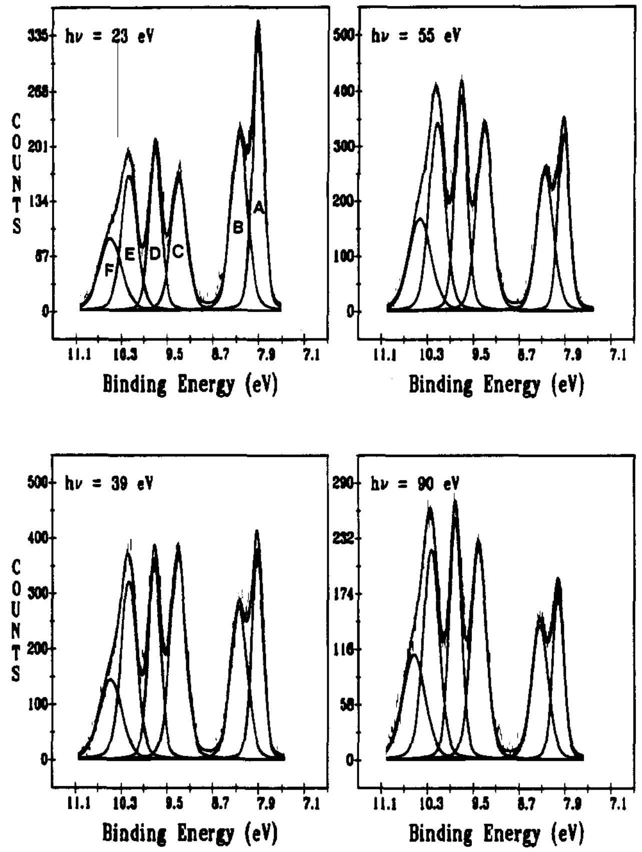

Figure 1. Photoelectron spectra of the upper valence MO's of CpPtMe$_3$ at 23-, 39-, 55-, and 90-eV photon energies.

In the previous conventional photoelectron studies, the spectrum of CpPtMe$_3$ was assigned largely on the basis of the Fenske–Hall calculations.[4b] From the Fenske–Hall predictions, bands A and B correspond to ionizations of the three nonbonding Pt 5d$_\pi$ orbitals (95% Pt 5d$_\pi$). Bands C and D are assigned to the Pt–Me σ orbitals, with $\sim$40% Pt 5d character in the orbitals giving rise to band C and with >70% Me σ character in band D. Bands E and F are assigned to the Pt–Cp orbitals with $\sim$75% Cp π character. The Fenske–Hall results for this molecule are in accord with the well-established, qualitative MO descriptions for molecules with general formula CpML$_3$, where M is a transition metal and L is an arbitrary ligand with only σ-donor capability.[16] This spectral assignment is also consistent with the previous conventional photoelectron studies of (cyclopentadienyl)methyl alkyls[17] and bis(cyclopentadienyl)methyl alkyls.[18] However, there were two factors that made us less than confident about the Fenske–Hall assignment for CpPtMe$_3$. First, the relative intensities of bands A and B decreased from the He I to He II spectra.[4b] Qualitatively, this decrease is not consistent with the Gelius model, because the atomic Pt 5d cross sections increase considerably relative to the ligand C 2p cross sections. Second, the ionization energies for the corresponding orbitals from CpPtMe$_3$ to the permethylated compound Cp*PtMe$_3$ (Cp* = η^5-C$_5$Me$_5$) shift very similarly. For example, bands A and B (from the Pt 5d$_\pi$ orbitals) decrease in ionization energies by 0.71 and 0.67 eV from CpPtMe$_3$ to Cp*PtMe$_3$, while bands E and F (from the Pt–Cp orbitals) decrease by 0.67 and 0.62 eV.[4b] In contrast, we would expect that the Cp-based orbitals would shift far more than the metal d orbitals.[19] For example, from CpMn(CO)$_3$ to Cp*Mn(CO)$_3$, the

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Table I. Xα–SW Results for $CpPtMe_3$ (C_s) Upper Valence Orbitals

	energy, eV[b]			charge distribution, %[a]				
MO (C_s)	theoret	exptl	assgnt	Pt 5d	Pt 6s	Pt 6p	Me	Cp
5a′	6.16	7.90	A	27.3	3.6	1.6	43.7	23.8
3a″	7.07	8.20	B	19.1	0.0	2.1	54.5	24.2
4a′	8.24	9.29	C	5.6	4.7	11.2	37.0	41.4
2a″	8.73			46.0	0.0	4.6	28.2	21.2
3a′	9.14	9.71	D	71.9	0.7	1.5	18.8	7.0
2a′	10.40	10.20	E	78.5	0.0	0.0	14.7	6.9
1a″	10.43			63.0	0.0	0.6	14.9	21.5
1a′	10.75	10.60	F	35.4	5.7	3.1	42.4	13.4

[a] In order to compare with the Fenske–Hall results,[4c] the charge distributions are not the usual atomic sphere charge contributions but rather the normalized atomic charges that approximately take into account the inter-sphere and outer-sphere charge densities by reproportioning them back onto the appropriate atomic spheres. [b] Calculated by the removal of a half of an electron from the HOMO (5a′).

ionization energy of the Cp π orbital decreases by 1.19 eV,[19a] while the ionization energy of the nonbonding Mn 3d orbitals decreases by 0.59 eV.

The above inconsistencies encouraged us to reconsider the assignment. We first performed Xα–SW calculations on $CpPtMe_3$, in an attempt to get better agreement between experimental and theoretical results. The Xα–SW results for the upper eight occupied MO's are presented in Table I. There are two very obvious qualitative differences between this calculation and the Fenske–Hall calculation. First, the Pt $5d_\pi$-based orbitals are unevenly sandwiched between the Pt–ligand σ orbitals in the Xα–SW calculation. Second, much more orbital mixing of the Pt, Me, and Cp orbitals is predicted in this calculation than in the Fenske–Hall result.

Considering Table I more closely, the three Pt $5d_\pi$-based MO's split into two sets: one consists of two nearly degenerate orbitals 1a″ and 2a′, formed by two of the Pt $5d_\pi$ orbitals back-donating their electrons into the e_2'' orbitals (e_2'' under D_{5h}; a′ + a″ under C_s) (see Table I); the other is the 3a′ orbital, formed by the filled–filled antibonding orbital interactions between one of the Pt $5d_\pi$ orbitals and the Cp a_2'' orbital (a_2'' under D_{5h}; a′ under C_s). This results in an energy gap of 1.3 eV between the two sets of the Pt $5d_\pi$-based MO's. It is also notable that significant Me character is mixed into the Pt $5d_\pi$ orbitals, presumably due to the ground-state distortion of the $PtMe_3$ fragment from a *fac*-ML_3 structure of an octahedral ML_6 molecule. The crystal structure of $CpPtMe_3$[20] indeed shows that the mean Me–Pt–Me angle is 85.4°, a 4.6° deviation from a ideal *fac*-ML_3 type of structure. Above the Pt $5d_\pi$-based MO's, there are four Pt–ligand (both Me and Cp) orbitals (2a″, 4a′, 3a″, and 5a′). Three MO's (2a″, 3a″, and 5a′) are formed by the Pt $5d_\sigma$ orbitals probably bonding to the Me σ orbitals but antibonding to the Cp e_1'' orbital, while the 4a′ orbital is formed by predominantly Pt 6p orbitals mixed with both Me and Cp ligand orbitals. Beneath the Pt $5d_\pi$-based MO's, there is the 1a′ MO consisting of the Pt $5d_\sigma$ (a′) orbital bonding to the Me σ and the Cp e_1'' orbitals.

The spectral assignment from the Xα–SW calculation is very different from that of the Fenske–Hall calculation (Table I, Figure 2). From the Xα–SW calculation, the ionizations of the Pt $5d_\pi$-based orbitals (3a′, 2a′ + 1a″ in Table I), with ~70% of Pt $5d_\pi$ character, give rise to bands D and E. The rest of the bands (A, B, C, F) are assigned to the Pt–ligand orbitals (5a′, 3a″, 4a′ + 2a″, 1a′), with mostly ligand character (70–80% in 5a′, 3a″) in bands A and B. This assignment gives a good rationalization of the experimental ionization shifts from $CpPtMe_3$ to Cp^*PtMe_3, which were observed in the previous He I spectra.[4b] For example, the similar ionization energy shifts of all bands upon ring permethylation[4b] can be explained in terms of the extensive mixing between the platinum and ligand orbitals in all upper valence MO's (Table I). The assignment of bands A and B to the ligand-based orbital ionizations is also consistent with the observations that the intensity of these two bands decreases as the photon energy increases (Figure 1). The electronic structure of $CpPtMe_3$ implied from this Xα–SW spectral assignment is obviously in contrast to the generally accepted description of the electronic structure of this type of molecule.[16]

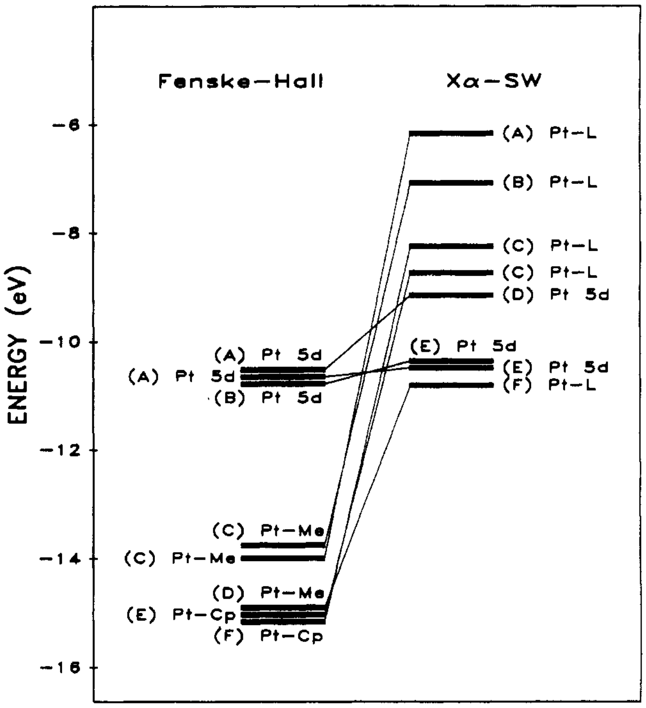

Figure 2. Spectral assignments from the Xα–SW and Fenske–Hall predictions. A–F correspond to the band labels in Figure 1. The ligand L includes both Me and Cp groups in the Xα–SW assignment.

To confirm the Xα–SW assignment, branching ratios from the experimental measurements and Xα–SW calculations are plotted in Figure 3. There is a satisfactory agreement of the branching ratios between the Xα–SW assignment (solid lines in Figure 3) and experimental measurements (asterisks) in the general trends and/or in the quantitative values for all of the six ionization bands. However, if the theoretical branching ratios are plotted according to the Fenske–Hall assignment by using the Xα orbital characters (dashed lines), the agreement is poor for bands A, C, and E, although a reasonable agreement is obtained for bands B, D, and F. For example, there is an error of about a factor of 2 between the Fenske–Hall branching ratios and the experimental measurements in the case of bands A and E. Also the branching ratios from the Fenske–Hall assignment show a decrease up to a photon energy of ~40 eV for band C whereas the opposite trend was observed experimentally. A contradiction between this assignment and the experimental measurement also exists in the general trend of the branching ratios below 40 eV for band A.

Furthermore, a comparison of the branching ratios between the Gelius model calculations and experimental measurements also supports the Xα–SW assignment, as shown in Figure 4. For the convenience of plotting, the branching ratios of bands D and

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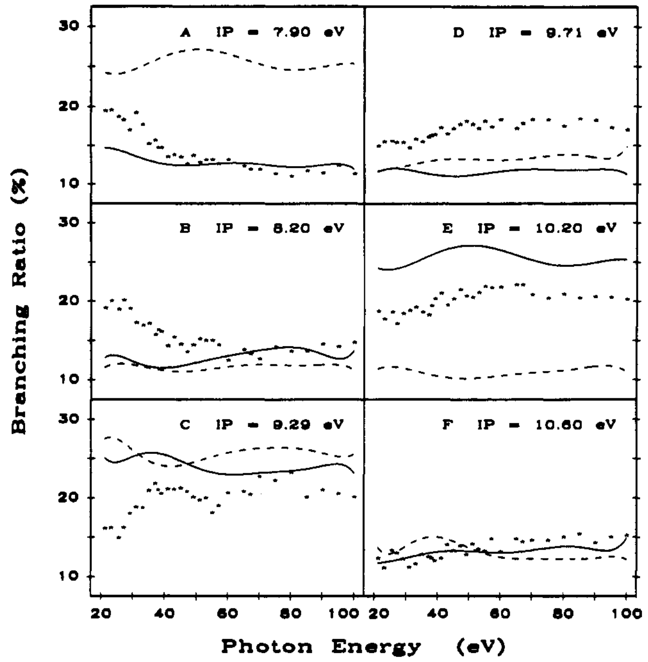

Figure 3. Branching ratios of the upper valence orbital ionizations of $CpPtMe_3$ from the experimental measurements (asterisks) and from theoretical calculations: $X\alpha$–SW assignment (solid lines); Fenske–Hall assignment (dashed lines). (See text.)

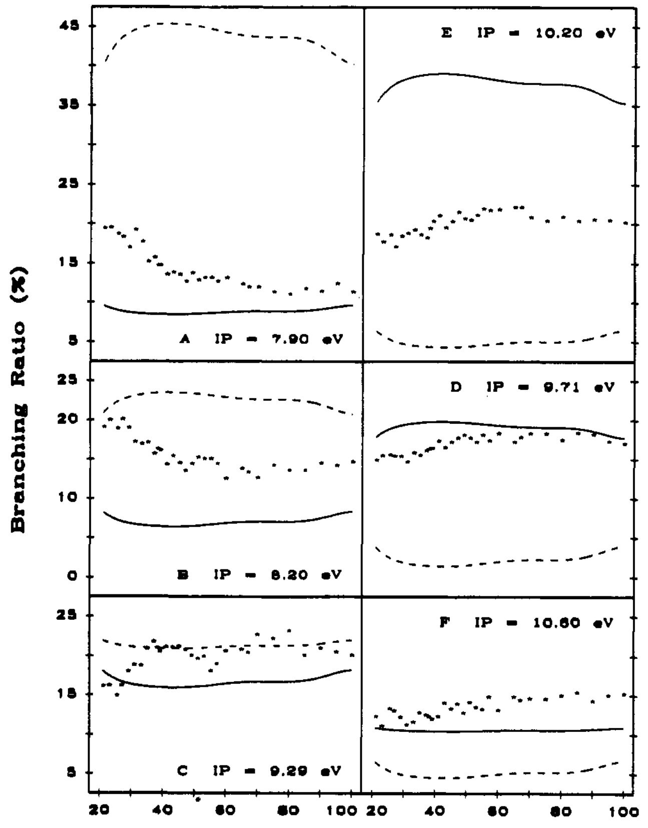

Figure 4. Branching ratios of the upper valence orbital ionizations of $CpPtMe_3$ from the experimental measurements (asterisks) and from the Gelius model calculations: $X\alpha$–SW assignment (solid lines); Fenske–Hall assignment (dashed lines). (The positions of bands D and E are switched; see text.)

E are switched in Figure 4. For these Gelius model calculations, the theoretical atomic cross sections (see Computational Details) were used along with the orbital characters from the Fenske–Hall and $X\alpha$–SW calculations. The Pt 6s and 6p cross section contributions were neglected because they are very small over the energy range of interest.[5] From Figure 4, it is immediately noticeable that the branching ratios from the Fenske–Hall and $X\alpha$–SW calculations are very different from each other for most bands. More importantly, there is reasonably good agreement between the $X\alpha$–SW and experimental results for bands A, C, D, and F, whereas the Fenske–Hall and experimental results are only in reasonable agreement for band C. For example, for bands A, D, E, and F, the Fenske–Hall and experimental results differ by factors between 2 and 4.

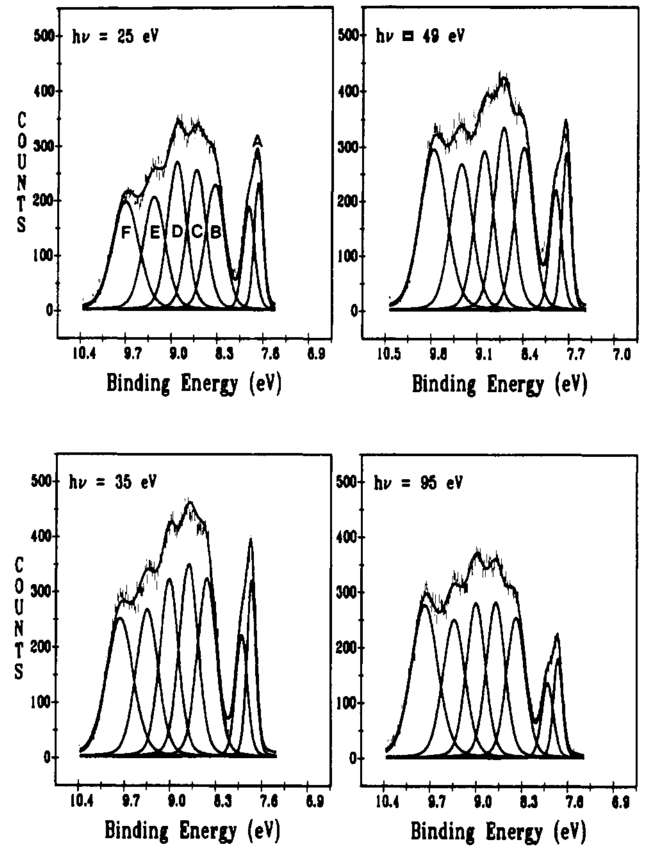

Figure 5. Photoelectron spectra of the upper valence MO's of $Me_2Pt(COD)$ at 25-, 35-, 59-, and 95-eV photon energies.

Taken together, Figures 3 and 4 give excellent evidence that the $X\alpha$–SW assignment is correct. In particular, these figures show that the Pt $5d_\pi$-based orbitals are *not* the HOMO's as the Fenske–Hall calculation suggests.

Finally, for the $X\alpha$–SW assignment, it should be pointed out that the overall agreement of the branching ratios between experimental measurements and the $X\alpha$–SW calculations are comparable with those between the measurements and Gelius model calculations (Figures 3 and 4). The reasonable agreement between the experimental and Gelius model values and the structureless branching ratios observed in the metal-based ionizations (D and E) indicate that there is no obvious resonance ionization mechanism in the Pt 5d-based orbital ionizations, in contrast to the previous observations for other organometallics.[21] This may be understood by considering the delocalization of the Pt 5d electrons (Table I). An interesting difference between the two methods is shown in band C for the $X\alpha$–SW assignment. The calculated ratios from the $X\alpha$–SW method show a structure similar to that from the experimental results (Figure 3), while those from the Gelius model show no structure. This probably originates from the neglect of the contribution due to the atomic orbital interactions in the Gelius model.[1]

(B) $Me_2Pt(COD)$. Spectra of the upper valence MO ionizations are shown in Figure 5 at photon energies 25, 35, 49, and 95 eV. The spectra at low photon energies are very similar to those

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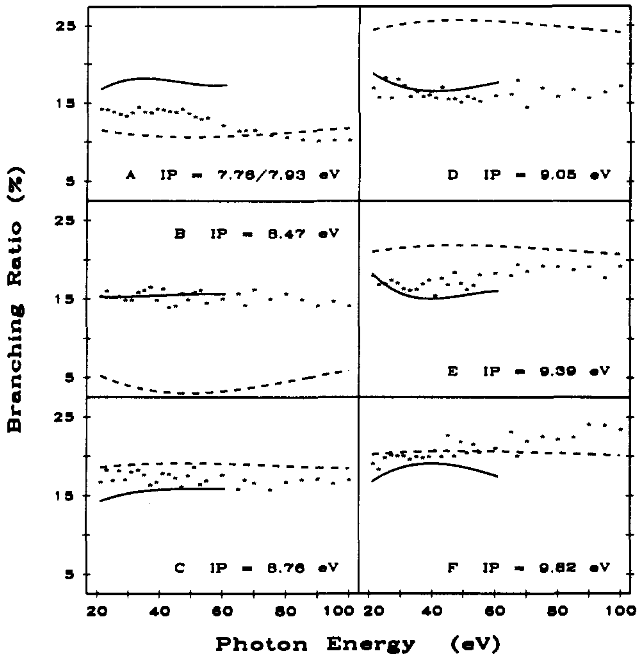

Figure 6. Branching ratios of the upper valence orbital ionizations of $Me_2Pt(COD)$ from the experimental measurements (asterisks) and $X\alpha$–SW (solid lines) and Gelius model (dashed lines) calculations. (See text.)

obtained with He I and He II radiations.[2a] At high energies ($h\nu$ > 55 eV), however, band A shows a relative intensity reduction. The experimental branching ratios are presented in Figure 6 along with the theoretical values from the $X\alpha$–SW and Gelius model calculations. The calculated ratios are based on the previous spectral assignment in which bands A and B were assigned to the ionizations from MO's with mostly C 2p character, while bands C–F were due to MO's with mostly Pt 5d character.[2a,c] Considering the observed similarity with $CpPtMe_3$, especially above 50 eV, and the computing cost, the $X\alpha$–SW ratios were calculated up to 61 eV only. There is a very good agreement between the experimental and $X\alpha$–SW ratios. The agreement between the experimental and Gelius model values is also satisfactory except for band B. Therefore, the comparison of the branching ratios supports the previous spectral assignment of this molecule.

Conclusions

Experimental and theoretical branching ratios strongly support the spectral assignment of the molecule $CpPtMe_3$ based on the $X\alpha$–SW calculations. The comparison of the observed branching ratios with those calculated with the Gelius model indicates that the intensity changes of the $CpPtMe_3$ valence ionization bands as a function of photon energy are largely associated with the Pt 5d and C 2p atomic cross sections. The $X\alpha$–SW assignment suggests that the eight upper filled valence MO's of $CpPtMe_3$ are composed of the three Pt 5d-based MO's being unevenly sandwiched between the Pt–ligand orbitals. Experimental and theoretical branching ratios also confirm our previous $X\alpha$–SW assignment for the $Me_2Pt(COD)$ valence ionizations and lend more confidence to the $X\alpha$–SW cross section calculations and molecular orbital assignments in organometallic Pt molecules.

Our new description of the electronic structure of $CpPtMe_3$ is clearly quite different from what has been generally accepted for $CpML_3$ molecules in general. Clearly, more molecular orbital calculations and photoelectron cross section studies are now needed on $CpML_3$ molecules.

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Solvent-Dependent Deuteron NMR Spectra and Solvatochromism in Ligand Field Absorption Bands for *trans*-$[CrX_2(3,2,3\text{-tet})]^+$: Correlation with the Angular Overlap Model Parametrization

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The solvent-dependent deuteron nuclear magnetic resonance (^2H NMR) and ligand field absorption spectra of *trans*-$[CrX_2(3,2,3\text{-tet})]^+$, where 3,2,3-tet denotes 1,10-diamino-4,7-diazadecane ($NH_2CH_2CH_2CH_2NHCD_2CD_2NHCH_2CH_2CH_2NH_2$) and where axial ligands X are F^-, Cl^-, Br^-, NCS^-, CN^-, OH^-, H_2O, and NH_3, were studied. These solvent dependencies were correlated with Gutmann's acceptor numbers for solvents. The ligand field bands were analyzed by using the angular overlap model, and it was found that the solvatochromism could be ascribed to variations of the metal–ligand σ-bond interactions (expressed by the $e_\sigma(X)$ and $e_\sigma(N)$ AOM parameter values) due to the selective solvation toward the axial ligands. A linear relation between the ^2H NMR shifts and the AOM e_σ parameters provides a direct probe to estimate the AOM e_σ parameter values. A notable ligand field variability was found and substantiated the interligand cooperative effect or cis electronic effect. This fact does not necessarily result either in rigorous parameter transferability from complex to complex or in additivity for mixed-ligand complexes.

Introduction

It is known that in general there is little solvent dependence of the ligand field d–d transitions in contrast to the noticeable solvatochromism in the charge-transfer transitions of metal complexes.[1] Recently, a solvatochromism was found for Co(III) and Cr(III) complexes with ethylenediamine-*N,N,N',N'*-tetraacetate (edta) type ligands,[2,3] which exhibited a fair correlation between the first d–d absorption band maxima and an acceptor number. This number was defined as a quantitative empirical electron-pair acceptor number for a solvent by Mayer, Gutmann, and Gerger[4] on the basis of the ^{31}P NMR chemical shift of tri-

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