dipole moment is in a perpendicular direction. Thus, for this $\pi\pi^*$ bpy transition there will be a small change in dipole moment for the metal complex if the bpy ligands are not symmetrically placed.

In Table III are some of the results of the calculation of the transition energies for bpy in its trans conformation, the conformation of bpy free in solution. In C_{2h} symmetry neither the ground state nor any excited states will have a dipole moment.[43] The lowest strong transition is at 35 950 cm^{-1}, and it is primarily long-axis-polarized with a transition dipole directed 4.82 D along the long axis and 1.08 D along the short axis. This transition is analogous to the long-axis transition in trans bpy, as both are primarily long-axis-polarized and represent primarily the promotion of an electron from the HOMO to the LUMO.

It is interesting that the slope of the E_{max} versus $F(n^2)$ plot of the $\pi\pi^*$ long-axis transition for free bpy lies within the values for the cis, exciton-coupled bpy ligands in the complexes reported. It thus appears that the dispersive effect of the solvent is qualitatively about the same for bpy in the two conformations. However, there is a large variation in the slope obtained for the cis bpy in the different metal complexes ((5.6–13.3) × 10^3 cm^{-1}). Thus, the specific nature of the coordination of the bpy has a significant influence on how its $\pi\pi^*$ long-axis transition is perturbed by the polarizability of the solvent.

Conclusion

Previous work has shown that the energy of the ^{1}MLCT transitions observed in the visible part of the spectrum shifts as a function of the solvent refractive index.[25] This was interpreted as consistent with the transitions being polar and leading directly to a single-ligand-localized charge-transfer state. Solvent shifts that are larger than those reported for the ^{1}MLCT absorptions are observed for the long-axis-polarized $^1\pi\pi^*$ absorption of bpy in metal complexes and free in solution and for the ^1L_a absorption of anthracene. It is concluded that the shifts in the absorption maximum with solvent refractive index for the ^{1}MLCT transitions do not show that this transition leads directly to a single-ligand-localized, C_2 symmetry state. Most evidence from other studies, such as from absorption polarization[18-20] and emission polarization[9,10,23] studies, are consistent with the ^{1}MLCT bands representing a delocalized transition. Thus, it seems reasonable to conclude that through most of the ^{1}MLCT visible bands the absorption is probably to a delocalized orbital and that both the ground and the initially populated excited states are symmetric. The nature of the absorption at the "red edge" of the visible bands is a matter of some discussion in the literature,[8-10,19,23] which the current work does not touch upon. While relevant to a description of the nature of the initial singlet produced, the current work does not reveal the details of the subsequent localization process.

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Electronic Structure of (η^5-C_5H_5)Pt(CH_3)$_3$ and (η^5-$C_5(CH_3)_5$)Pt(CH_3)$_3$ from UV Photoelectron Spectra

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Gas-phase He I and He II photoelectron spectra for CpPtMe$_3$ and the new complex Cp*PtMe$_3$ (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Me = CH_3) have been obtained. The valence orbitals responsible for the ionizations have been assigned to the corresponding molecular orbitals with the aid of Fenske–Hall molecular orbital calculations. The ordering of the molecular orbitals (in order of increasing binding energy) is Pt 5d < Pt–Me < Pt–Cp. From the photoelectron results, it is apparent that the Cp e_1'' orbitals interact strongly with the metal orbitals.

Introduction

Gas-phase UV photoelectron spectroscopy (PES) has proved an invaluable tool for studying the nature of the bonding between a central metal atom and the ancillary ligands of inorganic compounds.[1] PES has been useful for understanding the electronic structure of "sandwich" compounds[1b-d] and more recently has been extended to include "half-sandwich" or piano-stool compounds.[1d,e,2] In this second class of compounds, the metal is bound to a single carbocyclic ring, with the other ligands (either inorganic or organic) bound to the metal and comprising the "legs" of the stool. The ubiquitous η^5-cyclopentadienyl (Cp) ligand is the most common "bench" in these systems, and thus most of these studies have been devoted to metal cyclopentadienyl carbonyls and their derivatives. In contrast to metal cyclopentadienyl carbonyl compounds, metal cyclopentadienyl alkyls have not been examined in great detail.[2d] Because of differences in the bonding characteristics of carbonyl (a neutral π acceptor) versus alkyl (an anionic σ-only donor), significant changes between the electronic structures of these complexes may be expected. This perturbation is most evident in the high oxidation state of the metal generally found in cyclopentadienyl alkyl complexes.

There has been little activity regarding the chemistry of cyclopentadienylplatinum(IV) complexes. Robinson and Shaw first reported the synthesis of CpPtMe$_3$ and deduced from IR and NMR results that the compound was indeed a π complex,[3] a point later substantiated by X-ray structure analysis.[4] Maitlis has reported the synthesis of [Cp*PtBr$_3$PtCp*]Br$_3$, the structure of which was suggested to be an ionic triply bridged binuclear π complex.[5] Interest in chiral organometallic complexes prompted Shaver and co-workers to prepare (η^5-C_5H_5)Pt(CH_3)-

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Table I. Vertical Ionization Potentials, Bandwidths, Relative Intensities, and Assignments of the Photoelectron Spectra of $CpPtMe_3$ and Cp^*PtMe_3

compd	band	IP, eV	width, eV[a]	He I rel intens[b]	He II rel intens[b]	He II:HeI intens ratio[b]	assgnt
$CpPtMe_3$	A	7.90	0.25	1.23	1.08	0.88	Pt 5dπ
	B	8.20	0.39	1.30	1.20	0.92	
	C	9.29	0.34	1.25	1.47	1.18	Pt–Me(e σ)
	D	9.71	0.24	1.00	1.00	1.00	Pt–Me(a_1 σ)
	E	10.20	0.36	1.43	1.50	1.05	Pt–Cp(e_1'' π)
	F	10.60	0.49	1.09	1.12	1.03	
Cp^*PtMe_3	A	7.19	0.27	1.20	1.02	0.85	Pt 5dπ
	B	7.53	0.35	1.18	1.09	0.92	
	C	8.71	0.37	1.39	1.52	1.10	Pt–Me(e σ)
	D	9.14	0.22	1.00	1.00	1.00	Pt–Me(a_1 σ)
	E	9.53	0.35	1.40	1.39	0.99	Pt–Cp*(e_1'' π)
	F	9.98	0.49	1.39	1.33	0.96	

[a] Full width at half-maximum. [b] Referenced to band D.

$(CH_2CH_3)(C(O)CH_3)$, in addition to several polyfunctionalized $CpPt^{IV}$ complexes.[6] Photolysis of $CpPtMe_3$ in a variety of hydrocarbon solvents indicates homolytic cleavage of the Pt–Me bond to form methyl radicals and an unidentified platinum species.[7] It has been reported that η^5-cyclopentadienyltrialkylplatinum(IV) complexes are catalysts in the actinic radiation-activated hydrosilation of alkenes.[8] This reaction is applicable to both the formation of low molecular weight compounds and the curing of high molecular weight polymers containing unsaturated groups.

Fundamental studies of the electronic structure of these complexes should be important to understand the chemical properties exhibited. We therefore have undertaken a detailed UV photoelectron study of $CpPtMe_3$ and Cp^*PtMe_3. Elucidation of the electronic structure of this system is also facilitated through the use of Fenske–Hall molecular orbital calculations.

Experimental Section

Synthesis and Characterization. All synthetic manipulations were carried out under nitrogen by using standard Schlenk techniques. Melting points were measured in capillary tubes without correction. The ^1H NMR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ solutions. Mass spectra were obtained by electron impact on a Finnigan MAT 8230 spectrometer employing an ionization voltage of 70 eV. Elemental analysis was obtained from Guelph Chemical Laboratories Ltd.

The complex $CpPtMe_3$ was prepared by published procedures[3] and purified by vacuum sublimation. Purity was established by melting point, ^1H NMR spectroscopy, and mass spectrometry.

Cp^*PtMe_3 represents a new complex and was prepared as follows: 1,2,3,4,5-Pentamethylcyclopentadiene (0.243 g, 95%, 1.7 mmol) in dry THF (15 mL) was cooled to −78 °C. Into this solution was suringed *n*-butyllithium (0.65 mL, 2.6 M in hexane, 1.7 mmol). When the mixture was warmed to room temperature, white lithium pentamethylcyclopentadienide precipitated from the very bright yellow solution. The stirring suspension was cooled to −78 °C again, and finely powdered $[PtIMe_3]_4$[9] (0.50 g, 1.36 mmol) was added against a nitrogen counterstream. The mixture was slowly warmed to 50 °C (ca. 1 h), then stirred for an additional 2 h, and finally filtered. Solvent was removed from the filtrate by vacuum to yield an oily yellow residue. This residue was sublimed at 40 °C and 10^{-2} mmHg to yield a pale yellow solid (0.19 g, 37% yield). Mp: 90 °C. ^1H NMR ($CDCl_3$): δ 0.37 (s, ^2J(Pt–H) = 80.0 Hz, Pt–CH_3), 1.46 (s, ^3J(Pt–H) = 7.0 Hz, C_5Me_5–Pt). Molecular weight (mass spectrum): 375. Anal. Calcd for $C_{13}H_{24}Pt$: C, 41.62; H, 6.45. Found: C, 42.64; H, 6.76.

Photoelectron Spectroscopy. UV photoelectron spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer equipped with a hollow-cathode UV He lamp.[10] All spectra were obtained at a cell temperature of about 40 °C. The argon $^2P_{3/2}$ ionization at 15.76 eV was used as an internal calibration during data acquisition. The resolutions (fwhm of Ar $^2P_{3/2}$ ionization) were less than 0.027 and 0.036 eV for the He I and He II sources, respectively. Spectra were fitted to symmetric Lorentzian–Gaussian line shapes with the use of an iterative procedure.[11] The reproducibility of the vertical ionization energy (IE) is about ±0.02 eV. The relative band areas are reproducible to about 10% in the He I spectra and about 15% in the He II spectra. The band area ratios from He I and He II spectra were corrected for the electron analyzer transmission energy, by dividing by the kinetic energy of the band.

Computational Details. Molecular orbital calculations were performed on an IBM 3081-D computer system using the Fenske–Hall nonempirical approximate MO method.[12] All atomic basis functions were generated by the method of Bursten, Jensen, and Fenske.[13] Contracted double-ζ representations were used for the platinum 5d AO's as well as for the C 2p AO's. For platinum, the basis functions were derived for the Pt(IV) oxidation state, with the 4s exponent fixed at 2.00 and the 4p at 1.80.[14] An exponent of 1.16 was used for the hydrogen 1s AO.[15]

A fragment analysis was employed such that the MO diagram was constructed by the interaction of platinum with the valence orbitals of the Cp^- and Me_3 transformations. The Me_3 fragment was constructed from three CH_3^- transformations. Deletion of the Cp^- orbitals followed that as previously published.[16] The cyclopentadienyl ring was idealized to local D_{5h} symmetry, with the C–H bond lengths set to 1.08 Å. Each methyl group was idealized to local C_{3v} symmetry, as was the Me_3 fragment. Again, all C–H bond lengths were set to 1.08 Å. The geometry of the three-legged piano stool was idealized to C_s symmetry. The C–C (Cp), Pt–Cp(centroid), and Pt–Me bond lengths, as well as the Me–Pt–Me bond angle, used in the calculations are the reported mean values from the crystal structure.[4]

Results and Discussion

UV photoelectron spectra for $CpPtMe_3$ and Cp^*PtMe_3 are illustrated in Figures 1 and 2, respectively. The curve-fitting analysis for the valence bands in the low ionization energy region are reported in Table I. In the region from 11.5 to 16 eV, the spectra show complex unresolved bands that are assigned as arising from ionizations of the cyclopentadienyl ring σ and π a_2'' orbitals, as reported in the spectra of bis(cyclopentadienyl) complexes,[17] and from ionizations of the methyl σ_{C-H} bonding orbitals in metal alkyls.[18] A minimum number of peaks to adequately simulate this region have been fitted. These ionizations are not of sig-

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Table II. Molecular Orbital Energies and Mulliken Percent Character of the Upper Valence MO's

MO(C_s)	MO(C_{3v})[a]	ϵ, eV	band	% Pt 5d	% Pt 6s	% Pt 6p	% Me[b]	% Cp[c]
16a′	10e	−5.365		46.7	0.0	7.6	31.5	13.7
11a″		−5.383		46.7	0.0	7.6	31.5	13.6
15a′[d]	9e	−10.643		94.8	0.05	1.3	1.0	1.6
10a″		−10.644	A, B	94.1	0.0	1.5	1.2	1.9
14a′	6a$_1$	−10.649		97.9	0.35	0.3	0.2	0.6
9a″	8e	−13.905	C	40.6	0.0	7.1	50.8	1.5
13a′		−13.917		40.6	0.0	7.1	50.8	1.5
12a′	5a$_1$	−14.996	D	1.2	12.1	6.7	73.5	7.0
8a″	7e	−15.002	E, F	13.2	1.0	5.5	6.1	73.7
11a′		−15.006		14.0	0.2	5.5	1.1	78.5

[a] Symmetry label under "pseudo-C_{3v}" symmetry (see text). [b] CH_3 σ only. [c] Cp e$_1$″ π only. [d] HOMO.

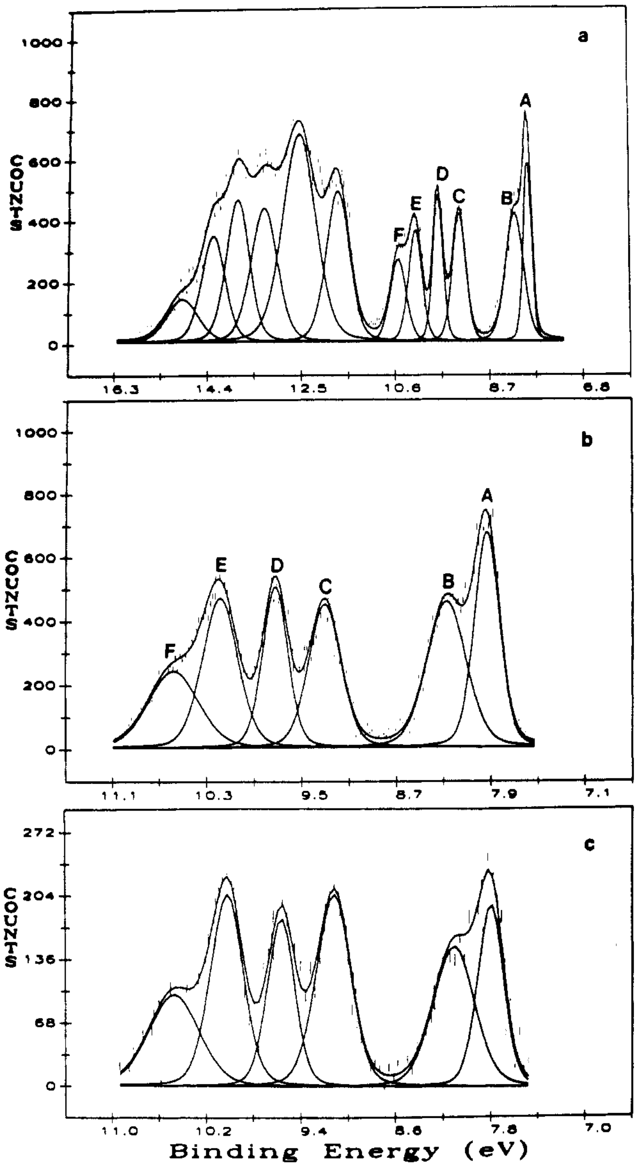

Figure 1. Full He I spectrum (a) and expansions of the low-energy region of He I (b) and He II (c) spectra of (η^5-C_5H_5)$PtMe_3$.

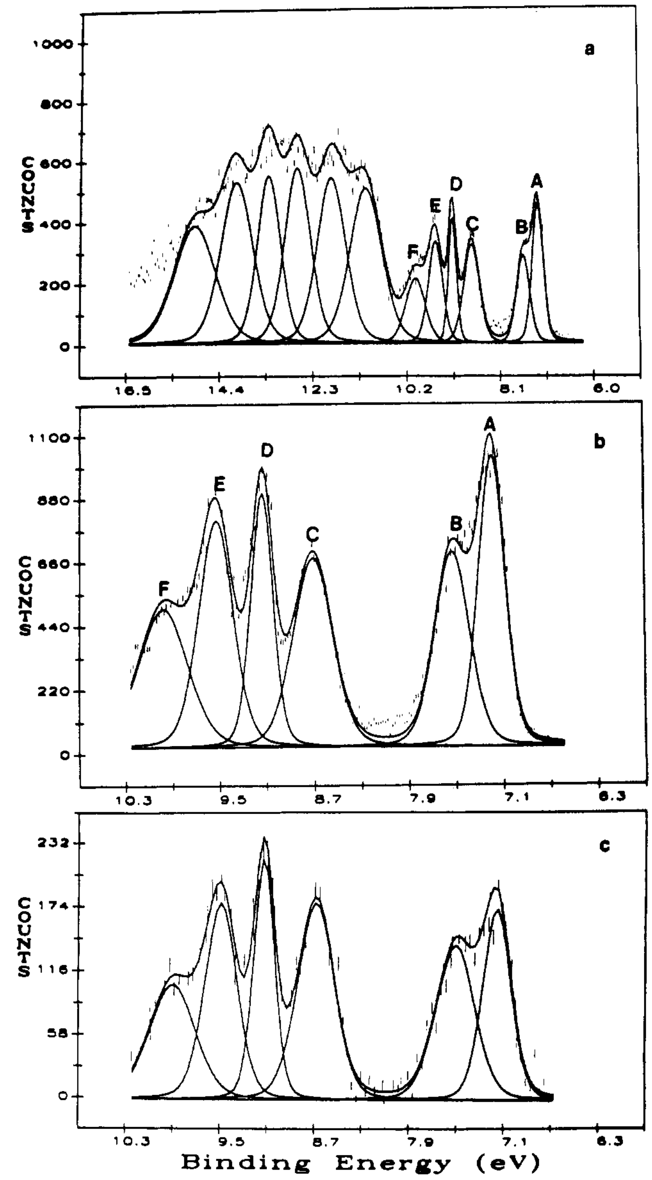

Figure 2. Full He I spectrum (a) and expansions of the low-energy region of He I (b) and He II (c) spectra of (η^5-C_5Me_5)$PtMe_3$.

nificance to the valence electronic structure and will not be discussed further. Cp*$PtMe_3$ (Figure 2) displays an additional band at 11.08 eV, which is associated with the ring methyl groups.[19] Ionization bands in the range of 7–10.5 eV are well resolved compared to those at higher energy. The first set of bands (A, B) is well separated from the subsequent bands (C–F). It is also evident that *all* of the bands in the 7–10.5-eV region are shifted by approximately 0.7 eV to lower energy upon ring permethylation, with bands C and D shifted to a slightly lower extent (0.55 eV). Similar features have been observed for other cyclopentadienylmetal complexes.[1,2] This is evidence for a largely inductive and hyperconjugative influence of the methyl groups on the electronic structure of the entire molecule.

The most striking feature in the low ionization energy region is that the He II:He I area ratios for all of the bands are not significantly different within the uncertainty of the curve-fit analysis. These bands (A–F) will receive primary attention in the subsequent discussion.

Molecular Orbital Calculation. The molecular orbital results for $CpPtMe_3$ are presented in Figure 3 and Table II. In order

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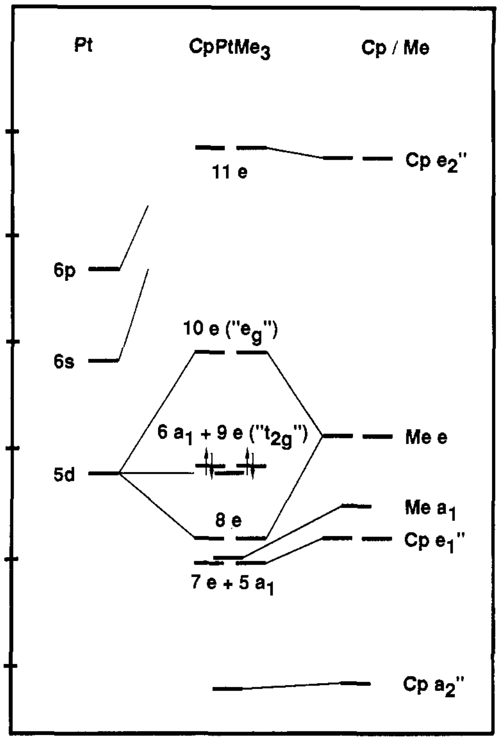

Figure 3. Orbital correlation diagram for $(\eta^5\text{-}C_5H_5)PtMe_3$.

to facilitate the assignment of the PE spectra, the calculation is presented as a platinum atom interacting with a Cp ring and the Me_3 ligand fragment. Our analysis will begin with a brief consideration of the $PtMe_3^+$ fragment and a comparison to other ML_3 fragments.[20]

The crystal structure of $CpPtMe_3$[4] shows that the mean Me–Pt–Me angle is 85.4°; i.e., the $PtMe_3^+$ fragment is nearly a *fac*-ML_3 fragment of an octahedral ML_6 complex. Reduction of symmetry from O_h to C_{3v}, without regard to the specific structure of the complex, demands that the Pt $5d\pi$ t_{2g} orbitals split as $a_1 + e$, the Pt $5d\sigma$ e_g orbitals as e, and the methyl group lone pairs as $a_1 + e$. However, it has been previously noted by several authors[2a,21-23] that when the L–M–L angles of an ML_3 fragment are close to 90°, the a_1 and e $d\pi$ orbitals are nearly degenerate, giving rise to a "pseudo-t_{2g}" set. As described by Elian and Hoffmann for carbonyl fragments, "the $M(CO)_3$ fragment 'remembers' its octahedral parentage, t_{2g} below e_g".[21] Replacement of CO with a σ-only ligand such as CH_3 does not alter this point. In fact, this idea can be extended further. For an octahedral complex of σ-only ligands, the $d\pi$ t_{2g} set is, by symmetry, unable to interact with these ligands. Similarly, in an octahedrally derived ML_3 fragment, the $d\pi$ orbitals can interact minimally with σ-only ligands L, even though there is no longer a symmetry restriction against their doing so. Thus, the a_1 and e $d\pi$ orbitals not only remain nearly degenerate but also are essentially nonbonding if L is a σ-only donor. This is evident in the calculation of the fragment $PtMe_3^+$, where the $a_1 + e$ $d\pi$ orbitals are ca. 99% Pt 5d.

"Capping" the ML_3 fragment with a Cp ligand does little to alter this qualitative picture.[24] The cylindrical symmetry of the Cp ligand, which is topologically similar to three cofacial ligands, preserves the octahedral geometry about the metal.[20,22d,25] The Cp e_1'' orbitals donate primarily into the higher lying empty $d\sigma$ e set of orbitals of the ML_3 fragment. For $PtMe_3^+$, these orbitals are oriented to readily accept the Cp "bench" to provide the piano-stool-structure symmetry.

The quantitative MO results for $CpPtMe_3$ are entirely in accord with the above discussion. The 5-fold symmetry of the Cp ring in combination with the 3-fold symmetry of either the Me_3 or $PtMe_3^+$ fragment results in a low (C_s) symmetry for the complex. However, since the same orbitals are degenerate under both 5- and 3-fold symmetry, it is more convenient to treat the molecule as "pseudo-C_{3v}". The MO diagram in Figure 3 uses this approximation, and its validity is evident in Table II. In Figure 3, it is observed that the CH_3 σ lone pairs form a_1 and e ligand group orbitals (for the Me_3 fragment), with the symmetric a_1 combination ca. 3.84 eV lower in energy than the antisymmetric e set. Whereas the Me_3 e σ set interacts strongly with the $5d\sigma$ orbitals on platinum to generate the 8e Pt–Me bonding orbital, the Me_3 a_1 σ combination interacts almost exclusively with the platinum 6s and $6p_z$ orbitals. Although the symmetry of the complex would allow interaction with the Pt $5d_{z^2}$ orbital, the geometry (wherein the CH_3 lone pairs nearly lie on the nodal surface of $5d_{z^2}$) dictates that this interaction is very small. Since the interaction of the a_1 ligand set with the higher lying Pt orbitals is not energetically favorable, the $5a_1$ Pt–Me bonding orbital is not as stabilized as much as the 8e. As indicated by the percent character in Table II, the Pt–Me $5a_1$ orbital contains less platinum character than the Pt–Me 8e orbital. Hence, the separation observed in $CpPtMe_3$ (1.085 eV) is considerably less than the separation of the ligand group orbitals.

The interactions of the Cp orbitals with platinum are quite straightforward. The Cp a_2'' π orbital (a_2'' under D_{5h}; a_1 under pseudo-C_{3v}) interacts only minimally with the platinum, largely because of its very low energy. The e_1 π orbitals (e_1'' under D_{5h}; e under pseudo-C_{3v}) interact with the Pt $5d\sigma$ orbital. This interaction generates the 7e molecular orbital, which is Cp–Pt bonding. The calculations place this orbital lower in energy than both the 8e and $5a_1$ Pt–Me bonding orbitals.

What remains are the Pt-based MO's of $CpPtMe_3$. The platinum 5d orbitals exhibit the familiar "two-above-three" splitting pattern exhibited for an "octahedral-like" three-legged piano stool. The $6a_1$ and 9e orbitals, which comprise the pseudo-t_{2g} set of orbitals, are only split by 0.0045 eV; i.e., they are nearly degenerate. As expected, there is virtually no ligand contribution, as indicated in Table II. For this diamagnetic d^6 Pt(IV) complex, the pseudo-t_{2g} set is filled, analogous to the highest occupied MO's of low-spin d^6 octahedral systems. The pseudo-e_g LUMO 10e consists of the Pt $5d\sigma$ and 6p orbitals, with antibonding contributions from both the Me_3 e σ and Cp e_1'' π orbitals. This leads to a HOMO/LUMO gap of 5.26 eV.

We have previously used the generation of a metal-localized nonbonding orbital to explain variable electron counts in $CpMLR_2$ (L = NO, O) complexes.[26] It was observed that, for a given oxidation state, the presence or absence of electrons in these nonbonding orbitals has little influence on the stability of the metal complex. Consistent with this notion, the d^0 complexes $CpTiMe_3$ and Cp^*TiMe_3 are readily synthesized.[27] Our MO calculation for $CpTiMe_3$ is virtually identical with that of $CpPtMe_3$, except, of course, that this complex has an unoccupied pseudo-t_{2g} set, as expected.[28] Within the comparison to octahedral complexes, these

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Ti(IV) complexes can be considered as three-legged piano-stool analogues of Wilkinson's homoleptic W(VI) alkyl complex WMe_6.[29]

Spectral Assignment and Interpretation. Since the spectra of both complexes in the low ionization energy region are very similar (see Figures 1 and 2 and Table I), the discussion that follows is applicable to both. The MO results will be particularly useful in the discussion that follows. For both compounds, the positions, relative intensities, band shapes, and splittings of bands E and F are unequivocally diagnostic for ionizations from the Cp and Cp* e_1'' π orbitals.[1e,2] For $CpPtMe_3$, this is the 7e molecular orbital (Figure 3). From the PES data, the splitting between bands E and F is 0.40 eV in $CpPtMe_3$ and 0.45 eV in Cp^*PtMe_3. This splitting is consistent with previous results for cyclopentadienyl- and (pentamethylcyclopentadienyl)metal carbonyls and their derivatives.[28] An explanation for this splitting has been advanced by Lichtenberger et al. in terms of the ground-state distortion of the Cp ring from D_{5h} symmetry.[2a] The solid structure for $CpPtMe_3$ indeed shows such a distortion in which two of the ring C–C bond lengths are 0.07 Å shorter than the mean value of the five ring C–C bonds.[4] As has been noted in other Cp–M photoelectron spectra, band F has a greater half-width than band E, but both bands have about the same area. Lichtenberger et al. have pointed out[1e,2] that the shortening of two ring C–C bonds increases the bonding capability of the one component of the Cp e_1'' π orbitals while decreasing the bonding capability of the other. This point is suggested by our calculations, wherein the two Pt 5dπ–Cp e_1'' overlaps are slightly different, even though the C–C bond lengths for the Cp ring are all equal in the calculation. Inasmuch as orbitals with more bonding character generally have broad vibrational envelopes,[30] the difference in half-widths between bands E and F is understandable.

The two well-resolved bands, C and D, which are located at lower ionization potentials than the Cp e_1'' ionizations, are readily assigned to ionizations from the Pt–Me $5a_1$ and 8e bonding MO's. This is also consistent with the lower shift in IE of these bands in the Cp* compared to the Cp derivative. Band C is considerably broader and more intense than band D. As is evident in Figures 1 and 2, band C shows a greater intensity enhancement upon He II irradiation. All of these observations are consistent with the assignment of band C as the more strongly Pt–Me-bonding 8e ionization, with band D due to the Pt–Me $5a_1$ ionization. The MO analysis (Figure 3) rationalizes the smaller binding energy of the 8e level compared to the $5a_1$ level. Since the compositions of the $5a_1$ and 8e MO's are quite different in terms of platinum character (Table II), their photoionization cross sections might be expected to be quite different. Indeed, the intensity ratio of band C to band D is clearly not 2:1 as would be expected from the orbital degeneracies and the simplest Gelius intensity model.[31] A similar result was found for the PE spectrum of WMe_6.[32]

This assignment of the metal–ligand ionization potentials in $CpPtMe_3$ (Pt–Me < Cp–Pt) is in complete accord with the Fenske–Hall MO results presented earlier. The relative energy order is also consistent with kinetic measurements on the decomposition of gaseous $CpPtMe_3$, in which the primary reaction step has been shown to involve formation of the methyl radical.[33] Metal–alkyl ionizations have been shown to be lower in energy than metal–cyclopentadienyl ionizations in previous studies of cyclopentadienylmetal alkyls[34] and bis(cyclopentadienyl)metal alkyls.[35] The ordering of these ionizations is apparently reversed (Cp e_1'' π < Ir–CH_3) in the PE spectra of Cp^*IrMe_4 and $Cp^*IrMe_2(OSMe_2)$, however.[2d] Fenske–Hall calculations on $CpIrMe_4$ indeed order the ionizations Ir 5d < Cp e_1'' π < Ir–Me σ.[36] Unfortunately, the ionizations of the Cp e_1'' π orbitals in these systems lie in a similar energy range as those found for the ionizations of M–C bonds, making absolute assignment difficult.[37-40]

Finally, there are the lowest energy ionization bands A and B, which are due to the Pt 5dπ orbitals. These ionization potentials (Table I) are comparable to those assigned to metal 5d electrons for a number of d^6 cyclopentadienyl-containing complexes of third-row transition elements.[2a,d,41] As discussed earlier, the $6a_1$ and 9e orbitals are nearly degenerate (splitting 0.0045 eV), consistent with the notion of a pseudo-t_{2g} set. The experimentally observed splitting of the A and B bands is consistent with the spin–orbit splitting of the "$^2T_{2g}$" hole state that would arise from $CpPtMe_3^+$. The observed separation, 0.32 ± 0.02 eV, is consistent with that seen for the T_{2g} state in $W(CO)_6$[42] but is only about half that observed in $CpRe(CO)_3$.[2a] The observed splitting is close to that of the spin–orbit coupling found in square-planar Pt(II) complexes[43,44] but is smaller than that of the free ion (0.50 eV),[45] as expected.[46] However, the relative intensities of bands A and B are not consistent with the spin–orbit splitting of a T_{2g} state as seen in $W(CO)_6$.[42] We might expect that spin–orbit coupling, which should only affect the ^2E state resulting from the ionization from a 3e electron, should yield three bands in the Pt 5d region. Because we only observe two peaks, and the widths (and thus intensities) of overlapping peaks A and B are not accurately determined by our symmetric peak shapes,[2a] it is very difficult to determine the relative position of the ^2E doublet and the $^2A_1$ singlet. We are inclined to place the a_1 ionization under the larger A peak.

Because metal d ionizations normally are enhanced in He II relative to He I spectra,[1,47] it is perhaps surprising that, for $CpPtMe_3$ and Cp^*PtMe_3, peaks A and B from the localized pseudo-t_{2g} Pt 5d set of orbitals show no intensity enhancement in the He II spectra (Figures 1 and 2; Table I) relative to other peaks (e.g. D–F) that result from orbitals with very little Pt 5d character (Table II). In contrast, for $CpMn(CO)_3$, the Mn 3dπ orbitals exhibit a large intensity enhancement for He II photons

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relative to that for He I.[2a] Although the atomic Pt 5d cross section (29.5 Mb at 21.2 eV and 31.3 Mb at 40.8 eV)[50] does not increase as much as most d cross sections from He I to He II photons, the large decrease in the C 2p cross section (6.1 Mb at 21.2 eV and 1.9 Mb at 40.8 eV) suggests that there should still be very large changes (up to a factor of 3) in He II:He I intensity ratios for peaks arising from orbitals of such widely different Pt 5d characters (Table II). However, recent results [e.g. for bis(π-allyl)nickel],[48] in which the Ni 3d cross section increases dramatically from He I to He II photons, show that He II:He I ratios cannot be used confidently for assigning metal d peaks, and there are at least two possible causes of the "anomalous" He II:He I ratios for our compounds. First, resonance effects (such as "shape" resonances) recently seen in synchrotron radiation studies in many molecules[49] can radically change relative intensities from those of the atomic Gelius treatment.[31] Second, changes in shape of the Pt 5d cross section as a function of photon energy from the atomic behavior[50] could give He II 5dπ intensities radically different from those expected on the atomic model. There has been considerable experimental[51] and theoretical[52] evidence that the shape of heavy-metal 5d cross sections are dependent on the chemical and physical state of the heavy metal. For example, the Pb 5d$_{5/2}$ cross-section maximum shifts from 37-eV kinetic energy for a thin Pb film on a Ni(110) surface[51b] to ~22 eV for bulk Pb. The shape of the 5d cross section is a function of the outgoing photoelectron f-wave phase shift, which is sensitive to the nuclear potential at the heavy metal.[52] Thus, if the maximum of the Pt 5d cross section shifts from ~25-eV kinetic energy in the atomic case[50] to ~10–15 eV in these Pt compounds, our anomalous He II:He I ratios could be readily rationalized. Synchrotron radiation studies are now required to confirm which of these two mechanisms is most important, but the second one seems more probable because all intensities remain relatively similar in He I and He II spectra.

Conclusions

In the complexes CpPtMe$_3$ and Cp*PtMe$_3$, the ionization energies of the filled valence molecular orbitals follow the order Pt 5d < Pt–Me < Cp–Pt. There is strong interaction between the platinum d$_{xz}$ and d$_{yz}$ orbitals with both the Cp e$_1''$ π and the Me$_3$ e σ sets. The conclusions based on our photoelectron study indicate that very effective covalent bonding is present in the high oxidation states of the heavy-transition-metal complexes.

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Transverse and Longitudinal Zeeman Effect on [PPh$_4$][FeCl$_4$]: Assignment of the Ligand Field Transitions and the Origin of the ^{6}A$_1$ Ground-State Zero-Field Splitting

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The spin-forbidden ligand field transitions of the high-spin ferric site in [PPh$_4$][FeCl$_4$] (D_{2d} symmetry) are definitively assigned through polarized single-crystal absorption, transverse Zeeman, and magnetic circular dichroism spectroscopies. A key feature of the magnetooptical experiments is the use of high magnetic field and low temperature to selectively populate the $M = {}^5/_2$ sublevel of the ^{6}A$_1$ ground state. The marked dependence of polarized intensity upon ground spin substate is due to the involvement of spin as well as orbital vector coupling coefficients in the selection rules derived for the spin–orbit intensity gaining mechanism. From the observed ^{4}T$_1$ axial splitting it is found that Griffith's theory relating the ^{6}A$_1$ ground-state zero-field splitting, D, to spin–orbit interactions with ^{4}T$_1$ excited states predicts the wrong sign of D. A modification to this theory is presented that includes the effect of anisotropic covalency in the σ-antibonding orbitals on the spin–orbit coupling matrix elements. The effect of covalency is further probed through the inability of the three-parameter ligand field theory to account for the experimental ligand field transition energies.

Introduction

A wide variety of proteins and enzymes contain ferric active sites that have high-spin d^5 electronic configurations. As these Fe^{3+} centers play a key role in biological processes, it is of importance to relate the spectral features of these active sites to their geometric and electronic structure.

The ultraviolet and visible absorption spectra of ferric complexes are dominated by intense, spin-allowed ligand to metal charge-transfer (CT) transitions. The ligand field (LF), or d–d, transitions have not been observed in proteins as they are all spin-forbidden and thus very weak. Energies for the LF transitions are predicted by the Tanabe–Sugano matrices.[1] In tetrahedral symmetry, the ground state is ^{6}A$_1$(t$_2^3$e^2) and the low-lying excited states in order of increasing energy are ^{4}T$_1^a$(t$_2^2$e^3), ^{4}T$_2^a$(t$_2^2$e^3), ^{4}A$_1$(t$_2^3$e^2), ^{4}E^a(t$_2^3$e^2), ^{4}T$_2^b$(t$_2^3$e^2), and ^{4}E^b(t$_2^3$e^2).

The ^{6}A$_1$ ground state for many Fe^{3+}-containing proteins has been probed by EPR spectroscopy.[2] The EPR spectrum for an $S = {}^5/_2$ ion in axial site symmetry is described by the spin Hamiltonian[3]

$$\mathcal{H} = g\beta H\cdot S + (a/6)(S_z^4 + S_x^4 + S_y^4) + DS_z^2 + (F/180)(S_z^4 - (30S(S+1) + 25)S_z^2) \quad (1)$$

The first term in eq 1 is the Zeeman splitting. Since there are no sextet excited states within the ligand field manifold available for spin–orbit (SO) coupling interactions, the g values are predicted by ligand field theory to be isotropic with the spin-only value of 2.0023. The parameter a is the zero-field splitting (ZFS) of ^{6}A$_1$ in cubic symmetry. As this term results from higher order interactions in spin–orbit coupling and cubic ligand field, it is predicted to be very small. If the symmetry is less than cubic, the axial ZFS parameter, D, will be nonzero and lift the degeneracy of the $M = \pm{}^1/_2$, $\pm{}^3/_2$, and $\pm{}^5/_2$ spin states by $2D$ and $4D$, respectively. The parameter F describes a higher order term in the axial distortion and is very small.

The goal of this study is to provide a basic understanding of the information content of these spectral features through a detailed single-crystal study of [PPh$_4$][FeCl$_4$]. In this compound the FeCl$_4^-$ complex occupies a site of rigorous S_4 crystallographic symmetry, with effective D_{2d} molecular symmetry.[4] The D_{2d}

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