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THE He(I) AND He(II) PHOTOELECTRON SPECTRA OF SOME η^5-CYCLOPENTADIENYL-TITANIUM, -ZIRCONIUM AND -HAFNIUM TRIHALIDE COMPLEXES

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Summary

The He(I) and He(II) photoelectron spectra are reported for $(\eta^5\text{-}C_5H_5)MX_3$ (M = Ti, Zr, Hf; X = Cl, Br) and some methylcyclopentadienyl and pentamethylcyclopentadienyl derivatives. Unambiguous assignments are made of the Cp orbitals, the halide a_2 and e orbitals. Very regular trends are observed in the ionization energies upon substitution of the ring, metals and ligands.

Introduction

In recent years much attention has been focussed on η^5-cyclopentadienyl-transition metal complexes. There are many reports on the photoelectron spectra of bis(η^5-cyclopentadienyl) complexes (sandwich compounds and bent complexes) and mono(η^5-cyclopentadienyl)carbonyl complexes and this work has been reviewed [1–3]. Variation of the ring systems also gave photoelectron spectra which could be interpreted on the same lines. Within the scope of our collaboration of η^5-cyclopentadienyl complexes [4] we were interested in the bonding properties of a series of compounds $CpMX_3$. One member of this series, $CpTiCl_3$, has been studied before [5].

We have interpreted the spectra of this series of compounds on the basis of empirical assignment criteria with special emphasis on He(I) and He(II) intensity differences.

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Experimental

Syntheses

All compounds are very air-sensitive, and the manipulations were done under nitrogen, using glove-box and Schlenk techniques.

The syntheses were performed following published procedures or modifications of these. For reasons of brevity, we will denote C_5H_5 by Cp, $C_5H_4CH_3$ by Cp′ and $C_5(CH_3)_5$ by Cp*.

$CpTiCl_3(Cp'TiCl_3)$ was prepared from $Cp_2TiCl_2(Cp'_2TiCl_2)$ and $TiCl_4$ [6]. $CpTiBr_3$ was made from Cp_2Mg and $TiBr_4$ [7]. $Cp'TiBr_3$ was prepared from $Cp'SiMe_3$ and $TiBr_4$ using a modification of a published procedure for $CpTiBr_3$ [8]. $Cp^{\star}MX_3$ ($X = Cl$; $M = Ti$, Zr, Hf; $X = Br$, $M = Ti$) were made from $Cp^{\star}Li$ and MX_4 [9].

All compounds were purified by sublimation (ca. 150°C, 0.1–0.001 mmHg) and identified by elemental analyses and IR and NMR spectroscopy.

Photoelectron spectra

The photoelectron spectra were recorded on a Perkin–Elmer PS18 spectrometer equipped with an Helectros Developments He(I)/He(II) hollow cathode source. The spectra of all complexes were obtained between 75 and 150°C. Ar and Xe were used as internal calibrants.

Theoretical model

Before discussing the spectra we will briefly review the relevant molecular orbitals for the compound $CpTiCl_3$. The other compounds can be treated analogously. We will implicitly assume the validity of Koopmans' theorem [10], i.e. each ionization will be associated with removing an electron from a canonical molecular orbital, with the ionization energy being the negative of the orbital energy of the corresponding molecular orbital.

X-Ray crystallography [11] has shown the compound $CpTiCl_3$ to consist of a pyramidal $TiCl_3$ unit with C_{3v} symmetry and a Cp-ring η^5-bonded to the Ti atom (Fig. 1). Formally, the Ti in this molecule can be considered as a Ti^{4+} ion, i.e. a Ti atom stripped of valence electrons. The 4^+ ion is surrounded by four univalent negative ions, three Cl^- and one Cp^-.

The three Cl^- ligands each possess three doubly occupied valence *p*-orbitals.

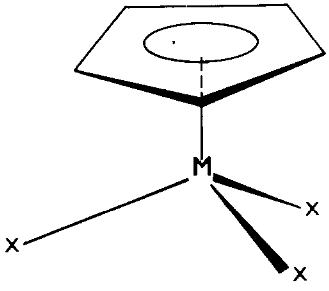

Fig. 1. The $CpTiCl_3$ molecule.

Since ionizations from halogen valence *s*-orbitals are not observed in photoelectron spectra, the total number of relevant valence orbitals on the $[Cl_3]^{3-}$ part is nine. These nine orbitals are depicted in Fig. 2. Three of these orbitals a_2 and e in Fig. 2a, b, c, are within the plane spanned by the three Cl atoms. Of these the a_2 combination contains three antibonding interactions. Thus, among the Cl-type orbitals this one is the highest in energy and most sensitive to changes in the Cl–Cl distances. The remaining six combinations of Cl-p-type orbitals can be divided in three along (Fig. 2d, e, f) and three perpendicular (Fig. 2g, h, k) to the Ti–Cl bonds. Both are $e + a_1$ combinations. The former three will mix with the empty Ti orbitals to affort Ti–Cl bonding.

Ionizations from chlorine (and other halogen) p orbitals can be recognized by the fact that they appear as sharp, intense bands in the He(I) but as nearly depleted bands in the He(II) spectra (due to the very poor cross section with He(II) photons). Molecular orbitals consisting of these atomic orbitals will show similar behaviour [12].

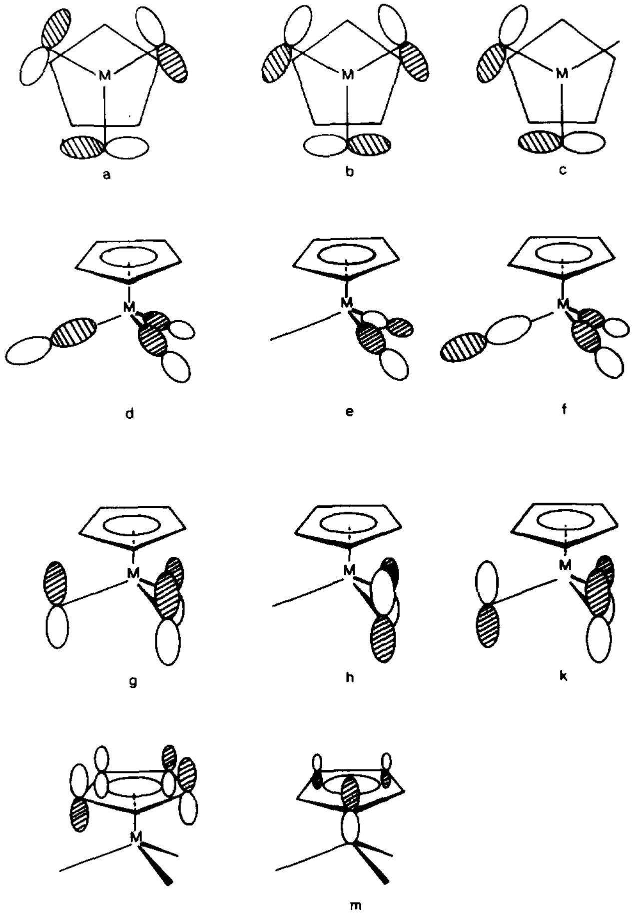

Fig. 2. The relevant valence orbitals of $CpMX_3$.

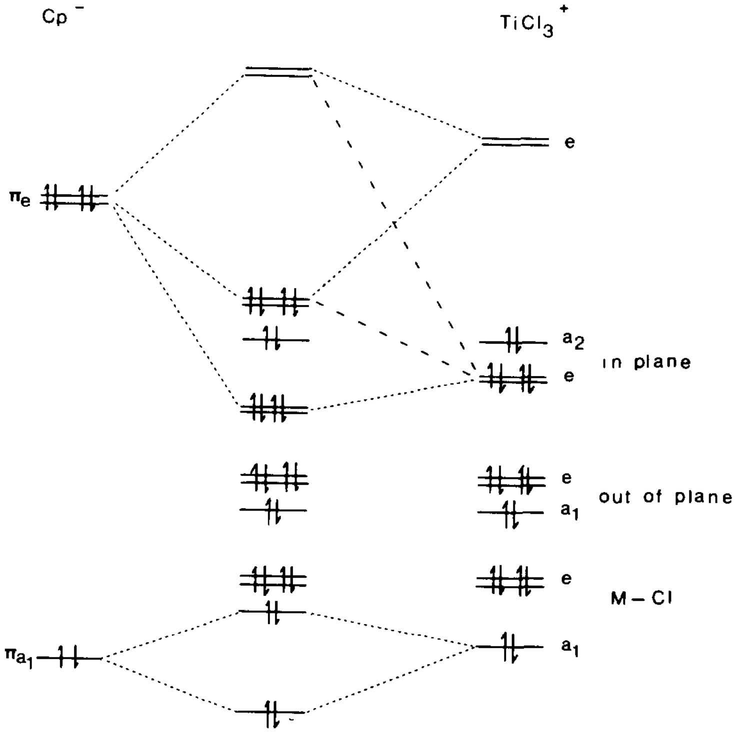

Fig. 3. MO diagram of $CpTiCl_3$.

The fourth formally negative part in the molecule is the $(C_5H_5)^-$ group. Its upper valence MO's are two degenerate π orbitals in the ring (Fig. 2 l, m). These will mix with Ti *d* and Ti *p* orbitals of proper symmetry to provide Cp–Ti bonding. Apart from this, the Cp moiety will give rise to ionizations from upper σ-orbitals and the a_2 π-orbital in the region > 12.5 eV.

He(II) cross sections for C_{2p}-type orbitals are slightly less than the He(I) cross sections, while CH σ-type molecular orbitals exhibit a much poorer He(II) than He(I) cross section. The He(I) and He(II) cross section for the Ti, Zr, Hf *d* orbitals both increase on going down the periodic system (heavy atom effect). In all cases, however, the He(II) cross section is larger than that for He(I) [13,14].

In Fig. 3, the interactions between the Cp^- and $(TiCl_3)^+$ fragments are displayed. As indicated, level interaction between orbitals of the same symmetry on the two parts (like *e*-type orbitals on Cp^- and $(TiCl_3)^+$) may be expected.

Results and discussions

$CpTiCl_3$ ($Cp = C_5H_5$, $C_5H_4CH_3$, $C_5(CH_3)_5$)

The spectra are shown in Figs. 4–6, and the ionization potentials are listed in Table 1. All spectra exhibit one band at lowest energy (having relatively large intensity in the He(II) spectra) which shifts strongly upon methyl substitution on the cyclopentadienyl moiety (vide infra). On the basis of this we assign this band to ionizations from the Cp-π orbital.

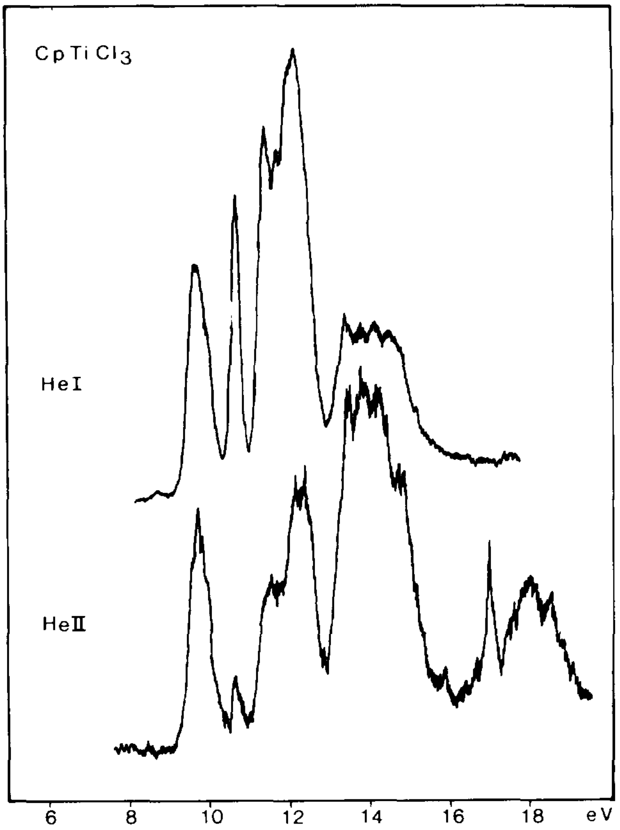

Fig. 4. He(I) and He(II) spectra of $\mathrm{CpTiCl_3}$.

The shifts upon methyl substitution (0.18 eV from Cp to Cp′ and 0.92 eV from Cp to $\mathrm{Cp}^{\star}$) can be treated with perturbation theory [15]. The theoretical value of about 1.5 eV for pure Cp orbitals agrees well with the actual value of 1.25 eV found for the e_{1u} orbital upon permethylation of metallocenes [1]. Since in metallocenes the e_{1u} orbital is unable to mix with metal *d* orbitals, this value of 1.25 eV will be the best approximation for the shift of a pure Cp-*e* orbital upon permethylation.

Since for the first band a shift of 0.92 eV is found upon permethylation, we may

TABLE 1

THE VERTICAL IONIZATION ENERGIES OF THE UPPER VALENCE BANDS [a]

Orbitals	Complexes							
	$\mathrm{CpTiCl_3}$	$\mathrm{Cp'TiCl_3}$	$\mathrm{Cp^{\star}TiCl_3}$	$\mathrm{Cp^{\star}ZrCl_3}$	$\mathrm{Cp^{\star}HfCl_3}$	$\mathrm{CpTiBr_3}$	$\mathrm{Cp'TiBr_3}$	$\mathrm{Cp^{\star}TiBr_3}$
Cp-*e*	9.79	9.61	8.87	8.71	8.65	9.38	9.16	8.59
X-a_2	10.77	10.66	10.39	10.80	10.81	9.88	9.70	9.47
X-*e*	11.64	11.34	10.70	10.97	11.03	10.74	10.49	9.87

[a] In eV.

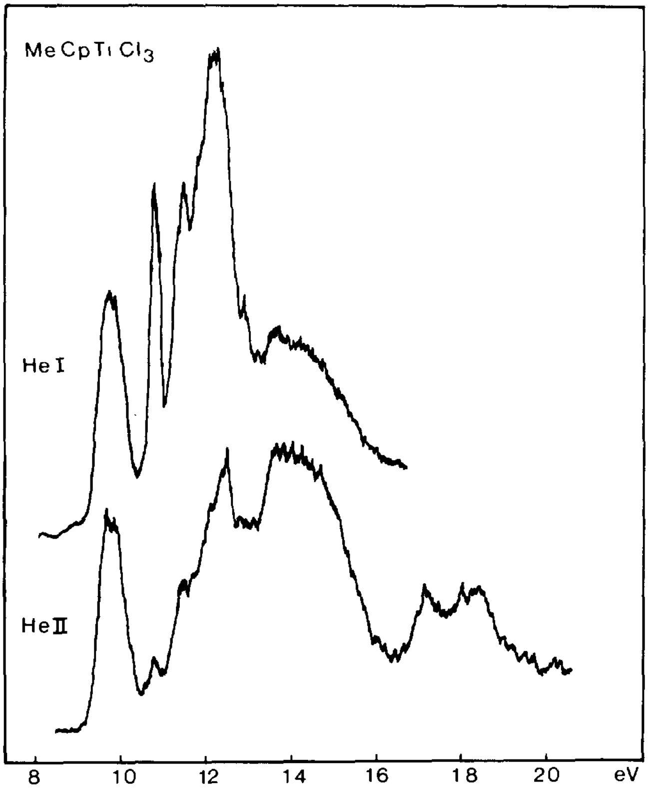

Fig. 5. He(I) and He(II) spectra of MeCpTiCl$_3$.

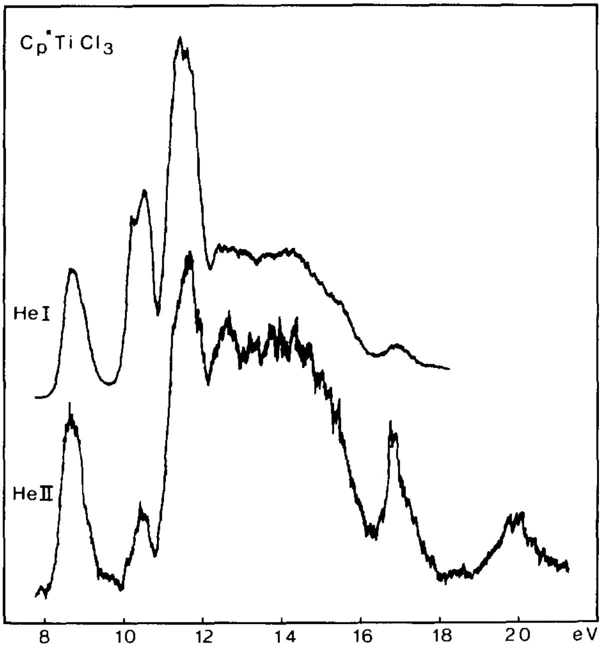

Fig. 6. He(I) and He(II) spectra of Cp*TiCl$_3$.

assume that this band arises from orbitals which have about 75% Cp-*e* character, and 25% of $(TiCl_3)^-$ character.

The second band in all the spectra (a shoulder in the spectrum of $Cp^{\star}TiCl_3$) is assigned as due to ionization from the a_2-in-plane-Cl lone pair type orbital on the basis of the following arguments:

(1) The He(I) intensity of this band is about half the intensity of the band assigned to Cp-*e* ionization. In view of the rather similar He(I) cross section for C_{2p} and Cl_{3p} orbitals [16] this suggests an ionization from a non-degenerate orbital.

(2) The very low He(II) intensity points strongly to high Cl character.

(3) The low IE value corresponds with the strongly antibonding character of this orbital (vide supra).

The third band in the spectra again exhibits a rather poor He(II) intensity, but in He(I) the intensity is about twice that of the second band. This suggests a halogen *e*-type ionization, probably the *e*-combination of *p*-orbitals out of the Cl–Cl–Cl plane and perpendicular to the M–Cl bond, since this corresponds to the normal ordering of Cl-type ionizations in MCl_3 units [13]. The shift of this band on permethylation is rather large (0.94 eV), which indicates a strong mixing with Cp orbitals. However, part of this shift comes from charge effects, as is indicated by the shift of the a_2 band (0.48 eV) from an orbital that can not mix with Cp orbitals. The remaining part of the shift (0.46 eV) brings us to postulate a strong interaction with the fragment Cp-*e* orbital. And indeed, addition of 0.46 and 0.92 eV of the experimental shift of this Cp-*e* orbital (vide supra) gives a total of 1.38 eV, which compares well with the value of a pure Cp-*e* ionization of 1.25 eV.

Next in the spectra is a rather broad band at about 12 eV. Upon methylation its maximum shifts about the same amount as the a_2 band, indicating pure charge effects. Because of this, and the position in the spectrum we assign this band to sundry Cl-type ionizations. Its relatively high He(II) intensity indicates mixing with Ti orbitals.

Higher up in the spectrum of $CpTiCl_3$ (> 12.5 eV) we find a broad band due to σ-Cp ionizations. The substitution of methyl groups for hydrogens on the cyclopentadienyl results in extra bands due to σ-type ionizations in the region 12–13 eV. The above assignment is at variance with an earlier assignment of $CpTiCl_3$ by Basso-Bart et al. [5]. Their assignment, based only on He(I) spectra and CNDO/2 calculations, must be contradicted. Their assignment of the second band in the spectrum to purely Cl orbitals of 8*e* and 7*a* symmetry can be rebutted by intensity arguments and by comparison with analogous Zr and Hf compounds (vide infra). Furthermore, these authors claim, on the basis of their CNDO/2 calculations, that only Cl-*e*-type orbitals at about 12.5 eV contain significant Cp-*e* character. This is in contrast to the measured shift of the third band in the spectrum upon methyl substitution (vide supra).

$CpTiBr_3$ ($Cp = C_5H_5$, $C_5H_4CH_3$, $C_5(CH_3)_5$)

The spectra are shown in Figs. 7–9, while the IE values are tabulated in Table 1. The general features in this series of spectra are the same as in those of the Cl compounds. Differences can largely be attributed to the difference in electronegativity between the halide ligands. The only important disparity is the relative energy of the band corresponding to the a_2 halogen lone pair orbital which is found at lower IP (about 0.9 eV). This could arise from the fact that the Br–Br distance in the

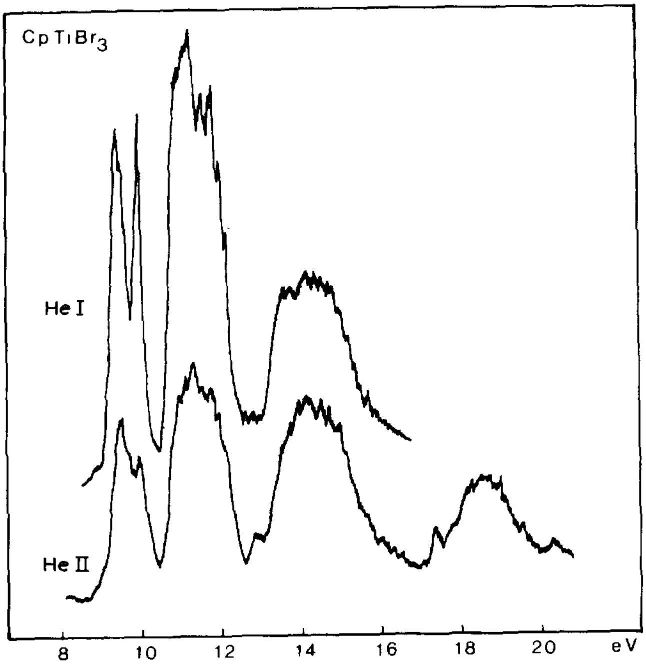

Fig. 7. He(I) and He(II) spectra of CpTiBr$_3$.

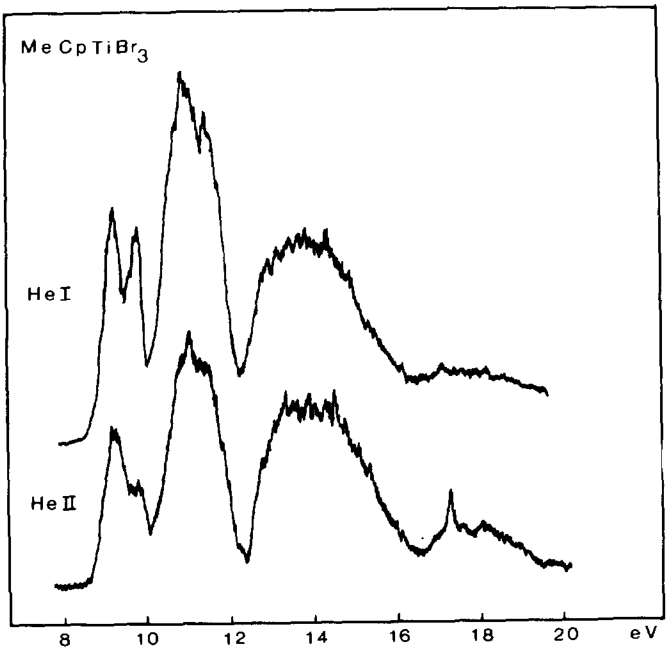

Fig. 8. He(I) and He(II) spectra of MeCpTiBr$_3$.

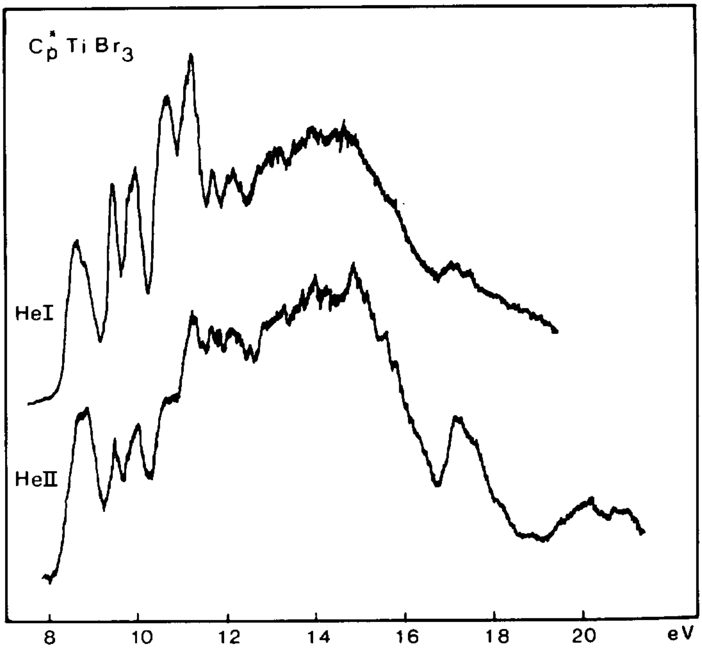

Fig. 9. He(I) and He(II) spectra of Cp*$TiBr_3$.

Br–Br–Br plane becomes relatively smaller than the Cl–Cl distances in the corresponding Cl compounds since the relative X–X distances in the planes, i.e. $(r_{Ti} + r_{Br})/(r_{Ti} + r_{Cl})$, is much smaller than the ratio r_{Br}/r_{Cl}. Therefore, assuming the X–Ti–X angles to be the same, the three antibonding interactions of the a_2 orbital will be larger in the Br series which will cause a destabilization of the a_2 bands in the spectra of the Br compounds.

Thus, whereas in the case of the chlorine compounds the a_2- and e-chlorine lone pair orbitals partly coincide upon pentamethylation, now the a_2 band is always separately visible as the first halogen type band in the spectrum. Since shifts upon methyl substitution in both series of compounds are about the same, we can conclude that the character of the valence orbitals also match i.e. the band at lowest IE is mainly Cp and the band at 10–10.5 eV mainly Br p-type, both mixed with each other and with metal orbitals.

*Cp**$ZrCl_3$ and *Cp**$HfCl_3$

The spectra of these compounds are given in Figs. 10 and 11 and the IE values in Table 1. The assignment of these spectra corresponds completely with that of the corresponding Ti complex. The shifts of the first two halogen bands in these spectra relative to the shifts in the Ti spectrum are in full agreement with the larger radius of the central atom forcing the halide ions further apart and lowering the energy of the a_2 and e orbital combination correspondingly. It may be noted that the strongest shift is observed on going from Ti to Zr. The ionic radii of Zr^{4+} and Hf^{4+} are about the same. Thus no significant shift is found on going from Zr to Hf.

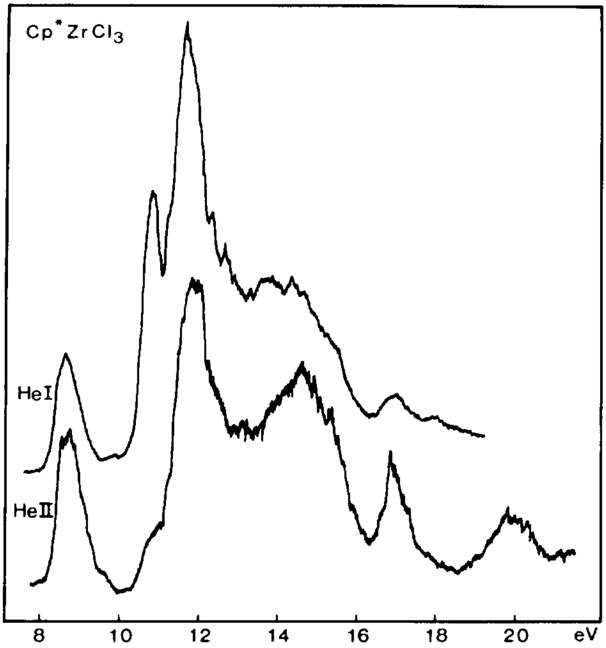

Fig. 10. He(I) and He(II) spectra of Cp*ZrCl$_3$.

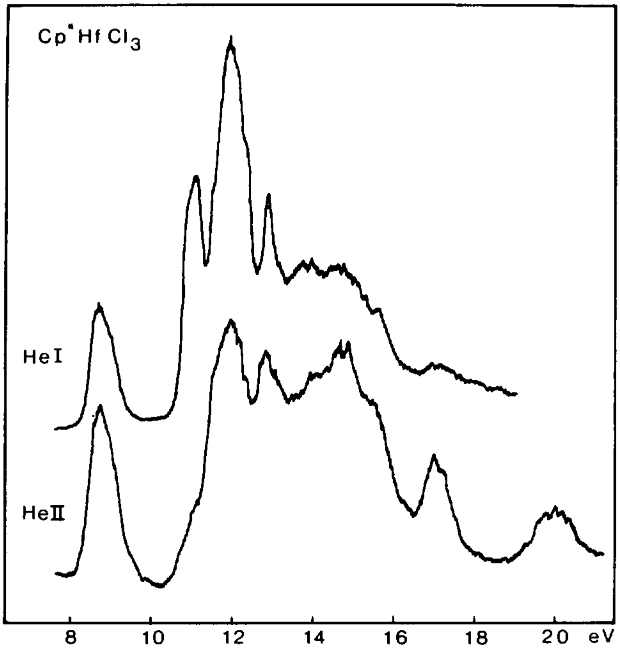

Fig. 11. He(I) and HE(II) spectra of Cp*HfCl$_3$.

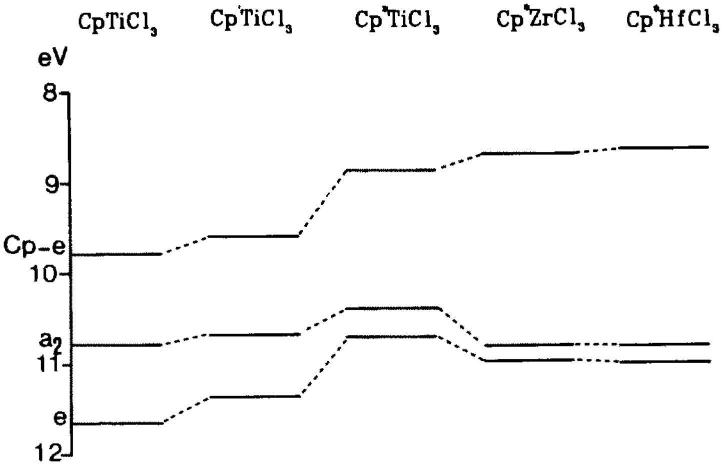

Fig. 12. Correlation diagram.

Conclusions

The assignment of the photoelectron spectra of the series $CpMX_3$ ($Cp = C_5H_5$, $C_5H_4CH_3$, $C_5(CH_3)_5$; M = Ti, Zr, Hf; X = Cl, Br) is straight-forward (as shown in the correlation diagram in Fig. 12), with the use of He(I)/He(II) intensity arguments, shift effects and arguments based on both the geometry of the compounds and the character of the valence orbitals. Mixing between Cp and *d*-type orbitals of the same symmetry is strong and about the same for the Cl and Br compounds.

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