

He(I) AND He(II) PHOTOELECTRON SPECTRA OF SOME MIXED SANDWICH COMPOUNDS OF TITANIUM, ZIRCONIUM AND HAFNIUM

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Summary

The He(I) and He(II) photoelectron spectra are reported for two series of transition metal mixed sandwich complexes of general formula L_aML_b ($M = \text{Ti}$, $L_a = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-CH}_3\text{C}_5\text{H}_4$, $\eta^5\text{-C}_5(\text{CH}_3)_5$; $M = \text{Zr}$, Hf , $L_a = \eta^5\text{-C}_5(\text{CH}_3)_5$; $L_b = \eta^7\text{-C}_7\text{H}_7$ (series I); $M = \text{Ti}$, $L_a = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$, $\eta^5\text{-C}_5(\text{CH}_3)_5$; $M = \text{Zr}$, $L_a = \eta^5\text{-C}_5(\text{CH}_3)_5$; $L_b = \eta^8\text{-C}_8\text{H}_8$ (series II)). Assignments were made of the metal d , cyclopentadienyl and carbocyclic π orbitals on the basis of He(I)/He(II) intensity ratios and shift effects and by comparison with UP data for related compounds. For series I no influence of the central metal upon the IEs of the highest occupied molecular orbital e_2 was observed. The IE of the non-bonding metal d_{z^2} orbital of Ti or Zr (5.28 and 4.70 eV, respectively) in the complexes of series II ($L_a = \eta^5\text{-C}_5(\text{CH}_3)_5$) is very low.

Introduction

During the last decade much attention has been focussed on η^5 -cyclopentadienyl transition metal complexes. There are many reports on the photoelectron spectra of bent and sandwich η^5 -cyclopentadienyl metal complexes with various ligands and the field has been reviewed by several authors [1–4].

As part of study of η^5 -cyclopentadienyl transition metal complexes [5,6a] we were interested in the bonding properties of a series of complexes CpML_b ($M = \text{Ti}$, Zr , Hf , $L_b = \eta^7\text{-C}_7\text{H}_7 = \text{Cht}$; $M = \text{Ti}$, Zr , $L_b = \eta^8\text{-C}_8\text{H}_8 = \text{Cot}$ [6b]). Ultraviolet

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photoelectron spectroscopy (UPS) seemed to offer the possibility of elucidating the electronic structure of these molecules, since many papers have dealt about the charge distribution in such mixed sandwich transition metal complexes. Photoelectron spectroscopy (ultraviolet [7,8] and X-ray [9]) is not the only method which has been used in elucidating the electronic structure of these molecules, however ^{13}C NMR [10], ESR [11] and semi-empirical and ab initio [15] molecular orbital (MO) calculations [12–14] having also been used in interpretation of their reactivity [16,17].

New aspects of the chemistry of the parent compound CpTiCht have recently been reported by Green et al. [18].

We now present the results of a UPS study of a complete series of low valence Group IVB ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) early transition metal complexes.

Experimental

Syntheses

CpTiCht , Cp^*TiCht , Cp^*MCht ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$), CpTiCot , Cp^*TiCot and Cp^*MCot ($\text{M} = \text{Ti}, \text{Zr}$) were prepared by published procedures [19]. Their identities were confirmed by elemental analysis (C, H, metal), mass spectrometry and IR and ^1H NMR or ESR spectroscopy.

Photoelectron spectra

The photoelectron spectra were recorded on Perkin–Elmer PS 18 spectrometer equipped with a Helectros Developments He(I)/He(II) hollow cathode light source. The spectra of all complexes were obtained between 85 and 155°C and calibrated against He, Ar and Xe as internal references.

Theoretical model

Before discussing the UP spectra we briefly consider the relevant molecular orbitals for the complexes CpTiCht and CpTiCot described earlier by Evans et al. [8]. The other compounds can be treated analogously.

We implicitly assume the validity of Koopman's theorem [20], i.e. each ionization will be associated with removal of an electron from a canonical MO, with the IE being the negative of the orbital energy of the corresponding MO.

X-ray diffraction studies on CpTiCht [21] and CpTiCot [22] show that the two rings are planar and parallel and so orbitals must be assigned in C_s , but for the ligands we make use of D_5 , D_7 and D_8 symmetry. It may reasonably be assumed that the other mixed sandwich compounds in these series have similar structures.

Although it is known that valence MOs of these mixed sandwich complexes involve contributions from metal and ligand AOs, it is often helpful in UPS studies [1–6,8] and even in MO calculations [12–14] to break-down the molecules into fragments and treat the complexes by the ligand field formalism. After discussion of this “formal theoretical model” and assignment of the UP spectra the real charge distributions can be considered.

CpTiCht

Formally the Ti can be considered in this molecule as a Ti^0 (d^4) atom surrounded by one Cp^- ion and one Cht^+ ion. This 16-electron complex has the

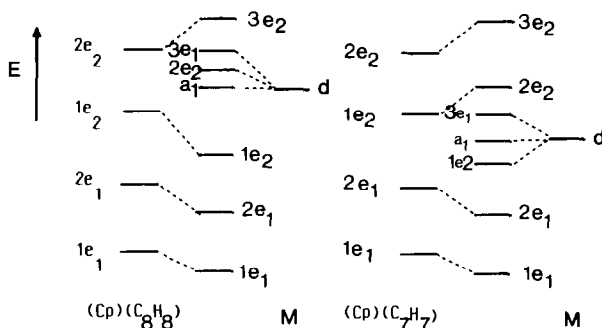


Fig. 1. Orbital scheme of $\text{CpM}(\eta^n\text{-C}_n\text{H}_n)$ ($n = 7,8$).

ground-state configuration $(e_2)^4$, as noted by Evans et al. [8], in the molecular orbital scheme of Fig. 1. This scheme has been the subject of calculations [12–14] and has been experimentally investigated [7].

The negative part of the molecule, the Cp^- moiety, has two degenerate π orbitals of the ring (e_1) and its characteristic position and shape of ionization energy is about 8.7–9.0 eV [1–4,23]. The formally positive part of the molecule, the Cht^+ moiety, has ionizations from e_1 orbitals at higher energies (> 10 eV) than those from the Cp ring owing to an increase of the ring size [24].

CpTiCot

Formally, Ti can be considered in this molecule as a Ti^{3+} (d^1)-ion as a result of two planar Hückel carbocyclic systems Cp^- and Cot^{2-} . This 17-electron complex has the ground-state configuration $(a_1)^1$ [8,25]. A Cot^{2-} moiety has its characteristic ionizations from π orbitals (e_1) at an energy of about 7.6 eV, as observed earlier [3,8], and the Cp^- moiety can be treated as above.

Substitution

Pentamethyl substitution in the Cp ring raises the energy of the ring π orbitals by about 0.92 eV on going from Cp to Cp^* , as has been observed before [5,6].

Cross-section

The He(I) and He(II) cross-sections for the pure Ti, Zr and Hf d orbitals both increase going down the periodic system (“heavy atom effect”). The He(I)/He(II) cross-section ratio becomes smaller in the range $3d \rightarrow 4d \rightarrow 5d$ [26].

Results and discussion

CpMChT ($\text{Cp} = \text{Cp}, \text{Cp}', \text{Cp}^*, \text{M} = \text{Ti}; \text{Cp} = \text{Cp}^*, \text{M} = \text{Zr}, \text{Hf}; \text{Cht} = \eta^7\text{-C}_7\text{H}_7$) [6b]

The He(I) and He(II) PE spectra of Cp^*MChT ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) are shown in Figs. 2–4 and the vertical ionization energies of the complete series are summarized in Table 1.

All the spectra exhibit the same pattern of bands, viz. three bands (indicated by A, B, C) in the valency ionization region (below 11.0 eV). Since for band A the

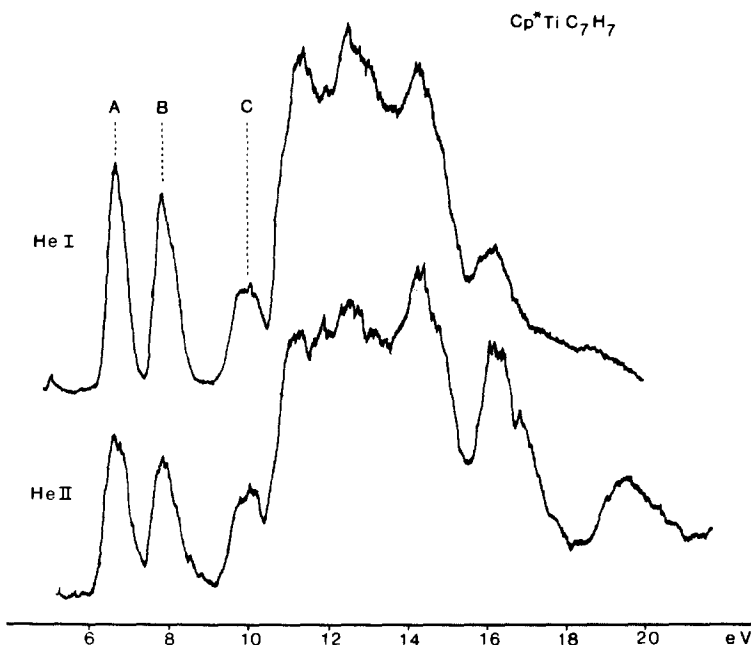


Fig. 2. He(I) and He(II) photoelectron spectra of Cp*TiCht.

He(I)/He(II) intensity ratios increase with respect to band **B** (Fig. 3) these bands must obviously be assigned to ionizations from $(e_2)^4$ with a substantial amount of the metal d -character. The IE of 6.70 eV in Cp*TiCht is 0.13 eV less than that

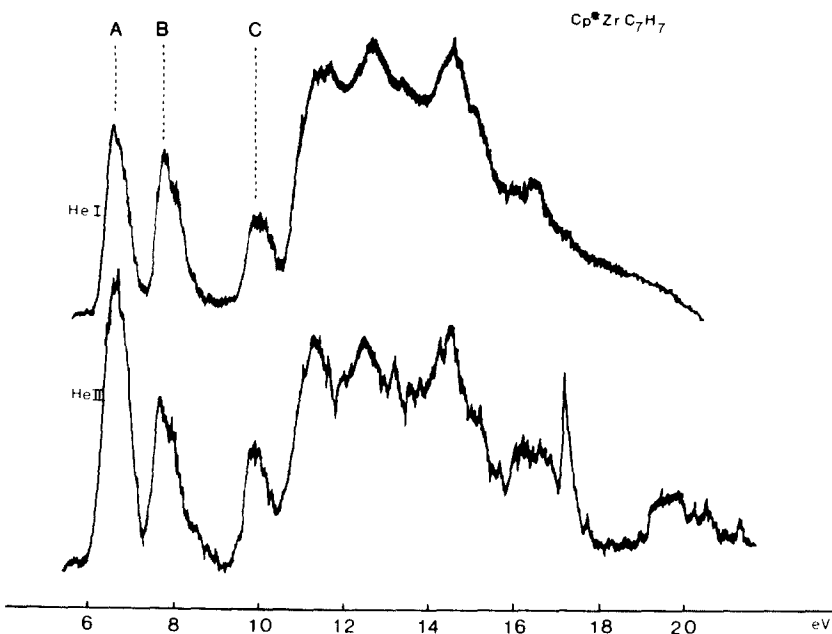


Fig. 3. He(I) and He(II) photoelectron spectra of Cp*ZrCht.

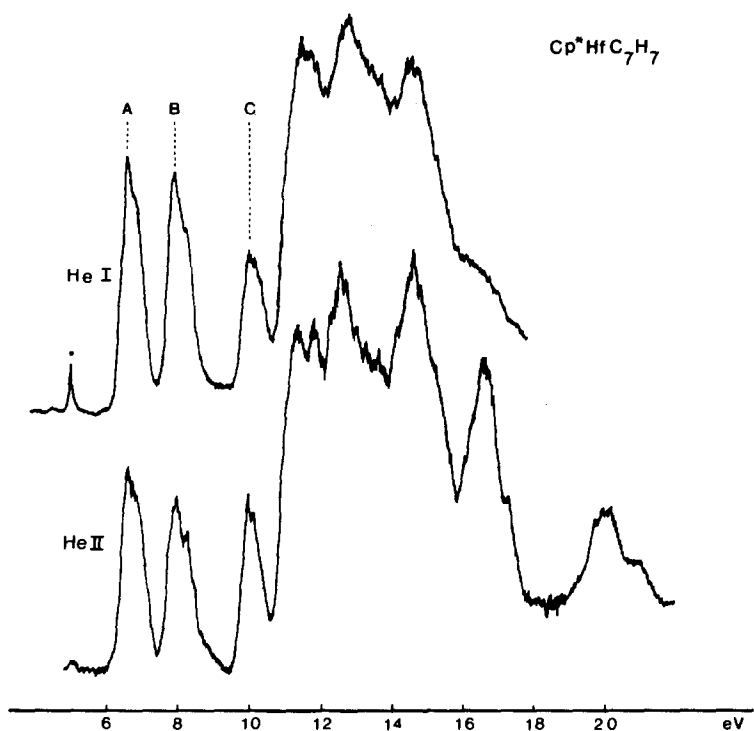


Fig. 4. He(I) and He(II) photoelectron spectra of $\text{Cp}^*\text{HfC}_7\text{H}_7$. The sharp band in the He(I) spectra indicated with an asterisk originate from He, which is ionized by He(II)- α radiation.

TABLE 1
OBSERVED VERTICAL IONIZATION ENERGIES FOR Cp_mMChT AND Cp_mCoT COMPLEXES

Compound	IE (eV) ^a			
		A	B	C
CpTiChT^b	(5.10) ^c	6.86	8.61	10.2
Cp^*TiChT	—	6.82	8.50	10.2
Cp^*TiCoT	(4.86) ^c	6.70	7.76	10.1
Cp^*ZrChT	(4.40) ^c	6.72	7.75	10.0
Cp^*HfChT	(4.07) ^c	6.67	7.78	9.9
	A	B	C	
CpTiCoT^b	5.67	7.62	8.63/8.93	10.5
Cp^*TiCoT	5.59	7.50	8.29/8.63	10.5
Cp^*TiCoT	5.28	7.54		10.5
Cp^*ZrCoT	4.70	7.66		10.5
Assignments	a_1	e_2 (ChT or CoT)	e_1 (Cp)	e_1 (ChT or CoT)

^a ± 0.05 eV. ^b Ref. 8. ^c These IEs have been calculated from the UV-VIS electronic absorption spectra: (a_1) \leftarrow (e_2) ref. 19a.

found for CpTiCht [8] owing to a small charge effect resulting from pentamethylation of the Cp-ring.

Bands **B** and **C** belong to the ionizations from the e_1 orbitals of the systems $(\text{Cp}^\star)^-$ and $(\text{Cht})^+$. Simple Hückel MO calculations on the isolated rings predict that the e -ring molecular orbitals become progressively more stable with increasing ring size [24]. With this and the fact that pentamethyl substitution in the Cp-ring gives a lowering of IEs of the pure e_1 -orbitals of about 1.25 eV [3] in mind, it is clear that band **B** must be assigned to the $\text{Cp}^\star e_1$ orbitals and band **C** to the Cht e_1 orbitals. As expected, the IE values arising from the Cht moiety show hardly any shift with respect to other metal complexes containing a Cht unit, 9.9–10.1 eV [1–4,8].

The IE values of the $\text{Cp}^\star e_1$ orbitals are raised by 0.95 eV with respect to Cp (e_1), which is in full agreement with our earlier measurements of 0.92 eV and represents only a minor deviation from the theoretical expected value of 1.24 eV [6]. This minor deviation can be attributed to some mixing of the metal d orbitals with the Cp (e_1) orbitals.

After a complete assignment of the UP spectra of $\text{Cp}^\star\text{TiCht}$ it is evident from Figs. 3 and 4 that the assignments for the two related complexes $\text{Cp}^\star\text{ZrCht}$ and $\text{Cp}^\star\text{HfCht}$ are the same.

We have thus completed this series of formally d^4 metal complexes containing the early transition metals Ti, Zr and Hf. The effect of changing the metal centre in $\text{Cp}^\star\text{MCht}$ by going down Group IVB is very small, as can be seen from Table 1.

The influence of the difference in electronegativity of Ti, Zr, Hf and of the size of the metal atom is evidently small (Table 1) in the UP spectra. In the case of the electronic absorption spectra, however, the influence of the metal changes is substantial, as was observed by Teuben et al. [19a]. The transition $(a_1) \leftarrow (e_2)$ shifts to higher energy, which must be attributed to an increase in energy of the $d(a_1)$ level, the LUMO. Obviously, the energy of the LUMO is sensitive to the radius of the metal atom, increasing as the radius increases.

CpMCot ($Cp = Cp, Cp', Cp^\star, M = \text{Ti}; Cp = Cp^\star, M = \text{Zr}; Cot = \eta^8\text{-C}_8\text{H}_8$) [6b]

The He(I) and He(II) PE spectra are shown in Figs. 5 and 6 for $M = \text{Ti}$ and Zr ($Cp = Cp^\star$) resp. The IEs of this series are listed in Table 1.

The basis of the assignment is the theoretical MO scheme of a 17-electron mixed sandwich complex (Fig. 1) in which the HOMO is the $(a_1)^1$ orbital. The presence of an unpaired electron has been confirmed by ESR [19a].

The two UP spectra exhibit two bands below 10 eV (**A** and **B**). At higher IE a very broad band is observed in which ionizations from ligand orbitals will participate. Band **A** can easily be assigned by comparison of the He(I) and He(II) spectra; the band increases in intensity significantly on going from He(I) to He(II) radiation, indicating large contributions from d orbitals. This, together with the band position [5] and the theoretical model (vide supra) points to assignment of band **A** to an ionization from the metal $(a_1)^1\text{-}d_{z^2}$ orbital. The IE value of this almost pure metal d orbital is in agreement with that reported for CpTiCot [8].

Bands **B** must be assigned to ionizations from ligand e -type orbitals of Cp^\star and Cot. In CpTiCot the ionizations from the two carbocyclic systems are separated by about 1 eV [8]. On pentamethyl substitution of the Cp-ring a destabilization of about 0.92 eV of the e_1 -ionizations is expected [3,6]. With this in mind it is not

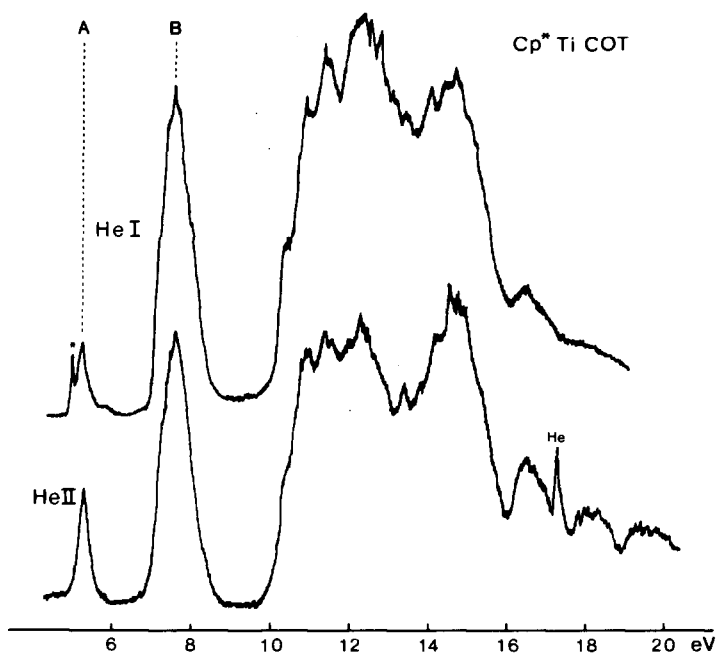


Fig. 5. He(I) and He(II) photoelectron spectra of Cp*TiCOT (* = He).

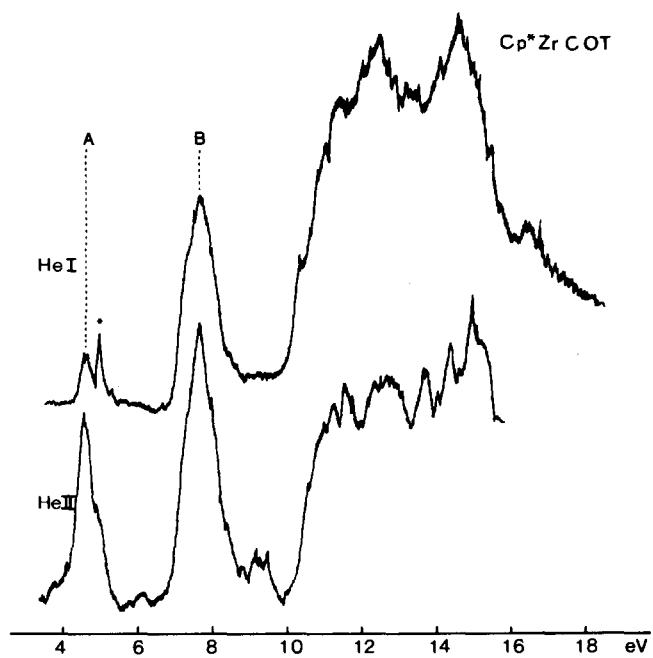


Fig. 6. He(I) and He(II) photoelectron spectra of Cp*ZrCOT (* = He).

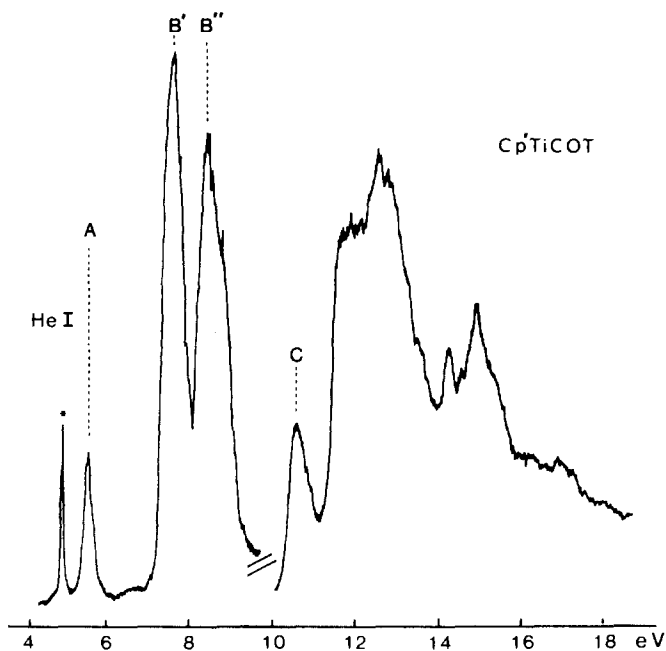


Fig. 7. Expanded He(I) photoelectron spectra of $\text{Cp}'\text{TiCot}$ ($' = \text{He}$).

surprising that in Cp^*MCot ($M = \text{Ti}, \text{Zr}$) the e_2 and e_1 ionizations of both rings coincide. To confirm the validity of this assignment we have measured the UP spectra of the monosubstituted $\text{Cp}'\text{TiCot}$ species (Fig. 7); since for this complex a destabilization of the e_1 -level by just 0.2 eV is expected, two separate bands should be detected, and this was found to be the case.

In contrast to the $(e_2)^4$ orbital in the CpMChT series, the $(a_1)^1$ orbital in the CpMCot series does vary with the metal in the series. This $(a_1)^1$ orbital is not strongly mixed with ligand orbitals and has a pure metal d nature. On going from Ti to Zr a destabilization of 0.58 eV was observed, as previously reported [28]. Cp^*ZrCot has one of the lowest recorded IE values, viz. 4.7 eV, recorded for an organometallic complex, and this is especially remarkable for an IE arising from a pure metal d_{z^2} orbital without ligand field splitting. The first IE for Cp^*HfCot can be expected to be lower.

Real charge distributions

With the formal charges of our theoretical model as starting point we now attempt to assess the real charge distributions in the molecules, with the aid of MO calculations and of the XPS, NMR and UPS data.

CpTiChT

Formally Cp is negative, Ti neutral, and ChT positive, but ab initio calculations and XPS measurements respectively indicate a charge of +1.75 [15] and +1.1 [9]

for the Ti-centre. This deviation from the formally zero oxidation state is a result of the charge redistribution with the two carbocyclic ligands. The electron population in the Cht ring is particularly underestimated. Instead of the charge of +1 on basis of the Hückel rule, ab initio calculations [13,15], XPS measurements [9] and ^{13}C [10] and ^1H [10,16] NMR values point to a net charge on the Cht ligand of about -1.0 as a result of π -backbonding from the metal.

The Cht ring in CpTiCht possesses even more negative charge than the Cp ring [9,10,13,15]. This charge difference is responsible for the fact that substitution reactions take place in the Cht ring rather than in the Cp ring as have been expected [16]. The mixing between the Cht e_2 orbitals and the Ti $3d$ orbitals was calculated to be 54 and 41% [15]. This mixing influences the cross section variation for band A on going from He(I) to He(II) excitation in Figs. 2–4.

It has been shown by others that the proportion of ring character in the e_2 orbital decreases with increase in the metal atomic number across the transition series [8,14,18]. Thus, on going from Ti to Hf in Cp^*MCht it can be expected that He(I)/He(II) cross section ratios will increase on going down the periodic table owing to a decrease of C_{2p} -participation in the $(e_2)^4$ orbital. This effect is clearly seen in Figs. 2 and 3 for $\text{M} = \text{Ti}, \text{Zr}$ respectively. On going to $\text{M} = \text{Hf}$, however, a second compensating effect has to be taken into account. In a study of a series of $\text{M}(\text{CO})_6$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) it was observed by Evans et al. [29] that there was no increase in the intensity He(I)/He(II) ratio for the t_{2g} ionizations on going to W from Cr and Mo compounds. This second compensating effect must be responsible for the decrease of the He(I)/He(II) intensity ratio of $(e_2)^4$ orbital in Cp^*HfCht compared to that for the Zr compound.

CpMCot

In the series Cp^*MCot ($\text{M} = \text{Ti}, \text{Zr}$) the real charge distributions differ from the theoretical model in which Cot was formally -2 and the metal centre formally $+3$. This formal picture of the electronic distribution is in agreement with literature findings and with our UP results. Thus, (i) Our UP results are consistent with a localized $(a_1)^1$ orbital as the HOMO; (ii) ESR spectroscopy confirms the paramagnetic nature; (iii) Clark and Warren [12] concluded from INDO SCF calculations for CpTiCot that there is hardly any mixing between the $3d$ orbitals on the Cot (e_2) orbitals (19%), which is in agreement with the formal oxidation state of $3+$; (iv) Clark and Warren [12] calculated a net charge on the metal of 0.275, which is in agreement with the results from XPS data obtained by Vlieg et al. [17]. In the present paper the charge on Ti in CpTiCot has been found to be 0.4. The negative charge on the Cot ring has been shown to be smaller than that on the Cht ring in CpTiCht . As a result, metallation by *n*-Bu-Li takes a different course for CpTiCot than for CpTiCht [16].

Conclusions

The assignments of the UV photoelectron spectra of the two series of mixed sandwich complexes are straightforward as is evident from the correlation diagram in Fig. 8.

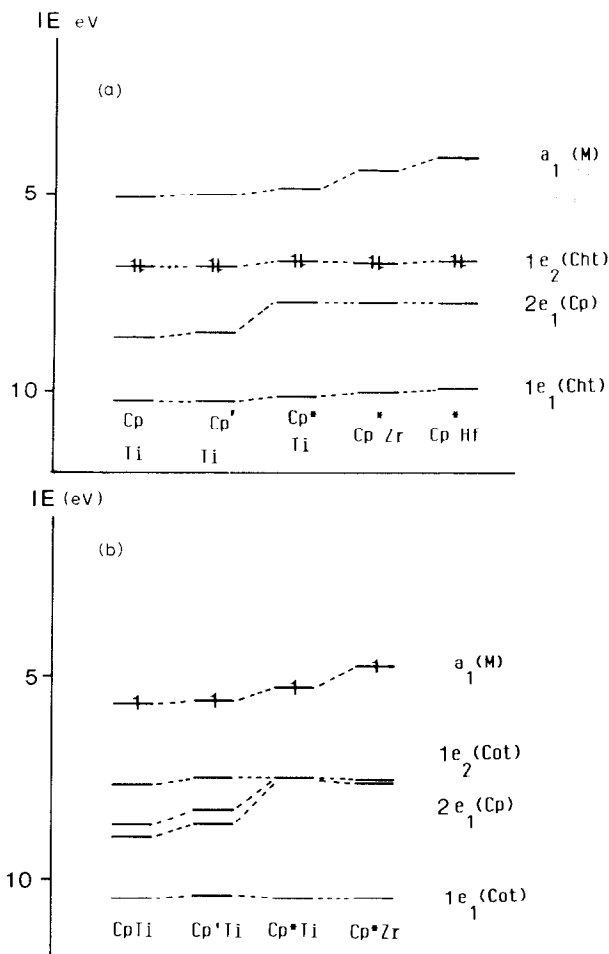


Fig. 8. Correlation diagram of the two series L_aML_b .

The charge distributions calculated by ab initio calculations are in agreement with UPS, XPS, NMR and ESR data.

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(b) Abbreviations used: Cp = $\eta^5-C_5H_5$, Cp' = $\eta^5-CH_3C_5H_4$, Cp* = $\eta^5-C_5(CH_3)_5$, Cht = $\eta^7-C_7H_7$, Cot = $\eta^8-C_8H_8$.
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