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Frontier occupied orbitals in methyl-substituted fulvene and dimethylenecyclopentenyltitanium complexes by UV-photoelectron spectroscopy and EHT calculations

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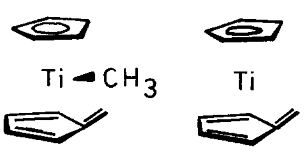
Abstract

UV photoelectron spectra have been obtained for $(\eta^5\text{-}C_5(CH_3)_5)(C_5(CH_3)_4CH_2)TiCH_3$ (Ia), $(\eta^5\text{-}C_5H(CH_3)_4)(C_5H(CH_3)_3CH_2)TiCH_3$ (Ib), $(\eta^5\text{-}C_5(CH_3)_5)(C_5(CH_3)_4CH_2)Ti$ (II), $(\eta^5\text{-}C_5(CH_3)_5)(C_5(CH_3)_3(CH_2)_2)Ti$ (III) and $(\eta^5\text{-}C_5H_2(CH_3)_3)_2Ti(CH_3)_2$ (IV) complexes and analyzed on the basis of extended Hückel-MO calculations. The exomethylene groups in fulvene and dimethylenecyclopentenyl ligands are π-coordinated. The HOMO in Ia, Ib, and III is delocalized over the methylene(s) containing ligand and the central atom, and has a bonding nature. The SOMO in II has predominantly the metal d-character. The calculated MO picture is consistent with the band shapes and relative band intensities observed in the low ionization energy region of the PE spectra.

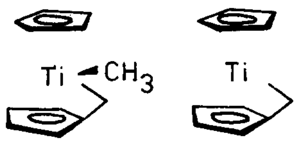
Introduction

Ultraviolet photoelectron (PE) spectroscopy has been successfully used in the investigation of the bonding in transition metal sandwich compounds [1]. Some PE spectroscopic studies of the Group IVB (Ti, Zr, Hf) sandwich complexes were concerned with d^4 bis-arene compounds [2] and mixed ligand d^2 and d^1 species [3,4]. The bent d^0 cyclopentadienyl complexes of the general formula Cp_2ML_2, where L is a halogen, pseudohalogen, alkylthio, or alkylseleno ligand, have been the subject of numerous theoretical and PE spectroscopic [5–12] investigations.

Series of methyl-substituted cyclopentadienyl derivatives were used to assign the PE spectra of Cp'_2TiX_2 ($Cp' = C_5Me_nH_{5-n}$; $n = 0$ (Cp), 1 (MeCp), 3 (Me_3Cp), 4 (Me_4Cp), 5 (Cp*)) [13] and $Cp'TiX_3$ [14] complexes. Similar study of Cp'_2TiMe_2 compounds has been hampered by the low stability of the Cp and MeCp derivatives on one hand and by ready elimination of methane from Me_4Cp and Cp* complexes at the temperatures required for the measurement of gas phase PE spectra [15]. This highly specific methane elimination is well known for $Cp^*_2TiMe_2$ and $(Me_4Cp)_2TiMe_2$, yielding Cp*Fv*TiMe (Ia) [16,17] and $(Me_4Cp)(Me_3Fv)TiMe$ (Ib) [18], respectively ($Fv^* = C_5(CH_3)_4CH_2$, $Me_3Fv = C_5H(CH_3)_3CH_2$). The tendency of the permethyltitanocene moiety to lose hydrogen was further demonstrated by the dehydrogenation of Cp^*_2Ti [19] and demethanation of Cp^*_2TiMe [20], both reactions yielding Cp*Fv*Ti (II). Furthermore, at higher temperatures Ia underwent loss of another molecule of methane, and II that of one hydrogen atom, both reactions giving the $\eta^3:\eta^4$-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl compound Cp*Ad*Ti (III) (allyldiene, $Ad^* = C_5(CH_3)_3(CH_2)_2$) [20]. The nature of the bonding of Fv* and Ad* ligand, and hence the valence state of titanium in II and III, has been the subject of a recent study [21], but the evidence is so far inconclusive. The fulvene ligand can be coordinated in Ia, Ib and II as a triene (**A**) or as a σ-bonded cyclopentadienyl methylene ligand (**B**):

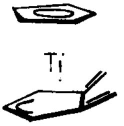


(A)

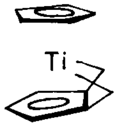


(B)

The IR [16,17] and the NMR spectral data [22] for Ia and the X-ray structure of the related complex $(\eta^5\text{-}C_5(CH_3)_5)(C_5(CH_3)_3(CH_2)CH_2\overline{CO(CH_3)C_6H_5)Ti}$ [20] show that the π-bonded methylene form (structure **A**) is favoured. Analogously the Ad* ligand in III can be π- or σ-bonded, as depicted in **C** and **D**. The coupling constants $^2J(HH)$ 4.4 and $^1J(CH)$ 160 Hz for the exomethylene groups in III indicate the presence of sp^2-hybridized methylene carbon atoms [20]. The NMR data for the allyldiene tungsten complex Cp*Ad*W [23] and the tantalum complex $Ad^*TaH_2(PMe_3)_2$ [24] are also consistent with the presence of π-coordinated exomethylene groups. The X-ray structure of the latter complex confirmed the adjacent position of the exomethylenes.



(C)



(D)

The compounds Ia, Ib and III are diamagnetic [16–18,20], which may indicate either Ti^{II} in singlet state or Ti^{IV}. The compound II is paramagnetic [19], which favours Ti^{III} (*vide infra*).

To throw light on the nature of the bonding in these complexes we have carried out a UV-PE study of Cp*Fv*TiMe (Ia), $(Me_4Cp)(Me_3Fv)TiMe$ (Ib), Cp*Fv*Ti (II) Cp*Ad*Ti (III), and $(Me_3Cp)_2TiMe_2$ (IV). The spectrum of the latter d^0 compound has been used to estimate the relative ordering of π(Cp) and σ(Ti–Me) based ionizations. Fragment MO-analysis based on the extended Hückel calculations of the non-methylated species is used for interpretation of the PE spectral features.

Experimental and computational details

Preparations

(*a*) Dimethyltitanocenes $Cp_2^*TiMe_2$, $(Me_4Cp)_2TiMe_2$ and $(Me_3Cp)_2TiMe_2$ were prepared by methylation of corresponding titanocene dichlorides with MeLi [17]. The compounds were identical with those described previously [18].

(*b*) The complexes Ia and Ib were prepared by thermolysis of the corresponding dimethyltitanocenes, and were identical with those described previously [18]. The ^1H and ^{13}C NMR spectra of Ib indicated the presence of one major and three minor isomers, containing the =CH– group in α- and β-position to the exomethylene group and on the same or opposite side of the molecular pseudoplane (given by centroids of Cp* and Fv* ligands and Ti atom) with respect to the Ti–Me bond which is out of the plane.

(*c*) Compound II was prepared as described previously [20]. A mixture of $Cp_2^*TiCl_2$ (1.12 g/2.88 mmol) and ^iPrMgCl (2.5 *M*, 1.5 ml/3.75 mmol) in diethyl ether was shaken until all the $Cp_2^*TiCl_2$ had dissolved. The ether was evaporated in vacuo and the Cp_2^*TiCl was extracted with hexane to give a blue solution. A solution of MeLi (1.6 *M* (Fluka), 1.8 ml/2.88 mmol) in ether was evaporated to dryness *in vacuo* and the hexane solution of Cp_2^*TiCl was added to the residue and the mixture was stirred for 2 h. The green solution was filtered to remove a yellowish solid and then evaporated to dryness *in vacuo*. Hexane was distilled into an attached 200 ml ampoule and the green, very soluble Cp_2^*TiMe was washed down to this ampoule by condensation of hexane vapours. Hexane was replaced by toluene (20 ml) and the solution was heated in the ampoule in an oven at 120 ° C for 4 h. The solvent and volatiles were distilled off *in vacuo* and the red solid residue was recrystallized from a minimum amount of hexane at low temperature.

*Cp*Fv*Ti (II):* The mass spectrum (direct inlet, 50 ° C) showed the molecular ion m/z 317 ($M^{+\cdot}$, 100%) and was further characterized by following ions in the order of decreasing intensity: $(M-H_2)^+ > (M-2H_2)^+ > m/z$ 119 $> (M-3H_2)^+ > (M-4H_2)^+$; ESR (toluene, 25 ° C): $g = 1.9520$, ΔH 7 mT; (toluene, −196 ° C): $g_1 = 1.9982$, $g_2 = 1.9870$, $g_3 = 1.8746$; $g_{av} = 1.953$; UV-VIS (hexane) λ_{max} 550 nm ($\epsilon \geqslant 2 \times 10^2$ cm^2 mmol^{-1}). All the data agree with those published [25]. Mass spectra, electronic absorption spectra and ESR spectra were recorded as recently described [18].

(*d*) Compound III was obtained by reduction of $Cp_2^*TiCl_2$ with $LiAlH_4$ in boiling toluene for 8 h followed by sublimation (100 °/10^{-3} torr) of the dirty green product [18]. Crystallization from hexane at low temperature yielded blue crystals. The ^1H and ^{13}C NMR spectra and mass spectrum of the product agreed with published data [20].

PE spectra

The PE spectra were recorded on a VG Scientific UVG 3 or a Perkin–Elmer PE 18 instrument. The samples were transferred into the spectrometers under an inert atmosphere. The working resolution (FWHM) was 30–50 meV on the Ar $2p_{3/2}$ band. The spectra were calibrated by reference to the Ar and Xe bands. A sufficient signal/noise ratio was obtained at temperatures 175 (Ia), 120 (Ib), 150 (II) and 100 ° C (III, IV).

Calculations

For the extended Hückel calculations the published H_{ii} values [5,26] and orbital exponents [27] were used. The titanium *d*-orbital was taken as the linear combination of two Slater functions [28]. The geometrical parameters are not available for I–III and the geometry was estimated from the X-ray diffraction data for the related fulvene complex [20] and Cp_2TiL_2 complexes [6,29,30]. The Ti $\cdots$ $CH_2(=C)$ and Ti $\cdots$ $C(=CH_2)$ distances were taken as 2.28 and 2.14 Å, respectively. For II and III a coplanar configuration of ligand planes and the C_s symmetry was assumed. The EHT method provides only qualitative and in principle empirical information, which has to be adjusted in the light of experience with analysis of structurally similar systems. The EHT results for the lowest ionization energies are usually qualitatively correct, but the order of the deeper levels may be considerably in error owing to the neglect of electron repulsion, reorganization, and correlation effects. More uncertain is the description of the open shell system II, for which the application of the Koopmans' theorem is even less justifiable. Similarly the calculated percentage localization does not indicate more than that the respective MO is localized more or less on the central atom.

Results and discussion

The PE spectra of I–IV can be divided into two principal regions. The poorly resolved broad features above ca. 10 eV originate in the obscuring by the ionization of σ(C–C) and σ(C–H) levels of the bands coming from the lowest ligand π-type orbitals. The low IE band system (< 10 eV) comes from the ligand π-orbitals and Ti–C-localized levels (Figs. 1–4). The vertical ionization energy (*IE*) values are summarized in Table 1.

$(Me_3Cp)_2TiMe_2$ (IV)

Two overlapping broad bands (**a**,**b**) are resolved below 10 eV (Fig. 1). These features no doubt include the ionizations from the cyclopentadienyl $e_{1g}(\pi)$ levels. By analogy with data for other $Cp_2M(CH_3)_2$ compounds (Zr [12], Mo, W [31]), the ionization of σ(Ti–C) orbitals can be assumed to fall within this region. It follows from the comparison with the PE spectrum of $(Cp^*)_2ZrMe_2$ and from the observed intensity ratio **b**/**a** that the shoulder **a** can be assigned to the $\sigma(Ti–CH_3)$ level and band **b** to the cyclopentadienyl π-orbitals. The *IE* of the cyclopentadienyl π-orbitals is approximately 0.2 eV lower than that for the corresponding dichloride [13], apparently because of the electron-releasing character of the methyl group.

Cp^*Fv^*TiMe (Ia) and $(Me_4Cp)(Me_3Fv)TiMe$ (Ib)

Four resolved features are observed in the low *IE* (< 10 eV) part of the PE spectra (Fig. 2). The vertical *IE* values for Ib are slightly higher than those for the permethylated species Ia. The relative band intensities suggest that features **b** and **c** come from more than two ionization events.

A useful way of describing the bonding in Ia and Ib is in the form of the diagram (Fig. 5) in which the MOs are derived by interaction between the orbitals of constitutive fragments. The LUMO of fulvene ($3b_1$) is strongly stabilized by the interaction with the central atom *d* orbitals. The C_1 symmetry of the Ti–fulvene

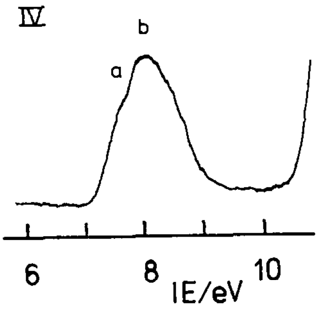


Fig. 1. HeI PE spectrum of $(Me_3Cp)_2TiMe_2$ (IV).

fragment rules out a straightforward description of orbital interactions such as that for the related Cp–metal fragment [32]. Nevertheless comparison with the orbitals of the MCp moiety shows that the $a_2(\pi)$ and $2b_1(\pi)$ orbitals of fulvene are analogous to $e_1(\pi)$ orbitals of cyclopentadienyl in so far as they are stabilized by the d_{xz} and d_{yz} orbitals (e_1 symmetry species). The overlap with the $d_{x^2-y^2}$, d_{xy} and d_{z^2} (e_2 and a_2 species) accounts for the strong stabilization of the $3b_1(\pi)$ orbital of fulvene. The HOMO in Ia and Ib correlates with the $3b_1(\pi)$ MO of fulvene. Comparison of the contour plots of this MO for the free and coordinated ligand indicates that the π-character of the CH_2=C bond is retained in the complex (Fig. 6). The same holds for the fulvene $2b_1(\pi)$ MO and the 27 MO of the complex (Fig. 7). The HOMO (32 MO) of the complex has a 32% contribution from the central atom orbitals (Table 2). The next three MOs (31–29) have π-ligand character and lie close in energy. The interaction scheme finds a counterpart in the PE spectra of Ia and Ib. Band **a** can be assigned to the ionization of the HOMO and the strong band **c** with the low energy side shoulder **b** to three ligand π MOs. The average destabilization of cyclopentadienyl π-orbitals per methyl

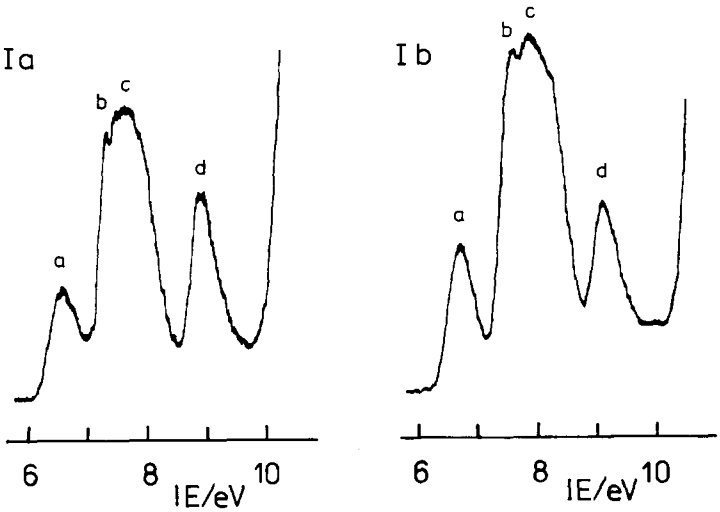


Fig. 2. HeI PE spectra of $(Me_4Cp)(Me_3Fv)TiCH_3$ (Ib) and Cp*Fv*TiMe (Ia).

Table 1

Vertical ionization energies of titanium sandwich complexes (eV)

Band	Ionization energy (eV)				
	$(Me_3Cp)_2TiMe_2$ (IV)	$(Me_4Cp)(Me_3Fv)TiMe$ (Ib)	Cp*Fv*TiMe (Ia)	Cp*Fv*Ti (II)	Cp*Ad*Ti (III)
a′				5.54 d(Ti)	
a	7.75 Ti–C(σ)	6.65 $3b_1(\pi)$ [a]	6.50 $3b_1(\pi)$ [a]	6.64 $3b_1(\pi)$	6.55 $3b_1(\pi)$
b	8.07 Cp(π)	7.55 $a_2(\pi)$+Cp(π)+Ti–C(σ)	7.41 $a_2(\pi)$+Cp(π)+Ti–C(σ)	7.53 $a_2(\pi)$+Cp(π)	6.96 $2a_2(\pi)$
c		7.86	7.63	7.71	7.52 Cp(π)
d		9.03 $2b_1(\pi)$	8.93 $2b_1(\pi)$	7.87	7.84 Cp(π)
e				8.94 $2b_1(\pi)$	8.91 $a_2(\pi)+2b_1(\pi)$

[a] The levels having the largest contribution from the fulvene and the allyldiene ligand are classified by the C_{2v} symmetry species.

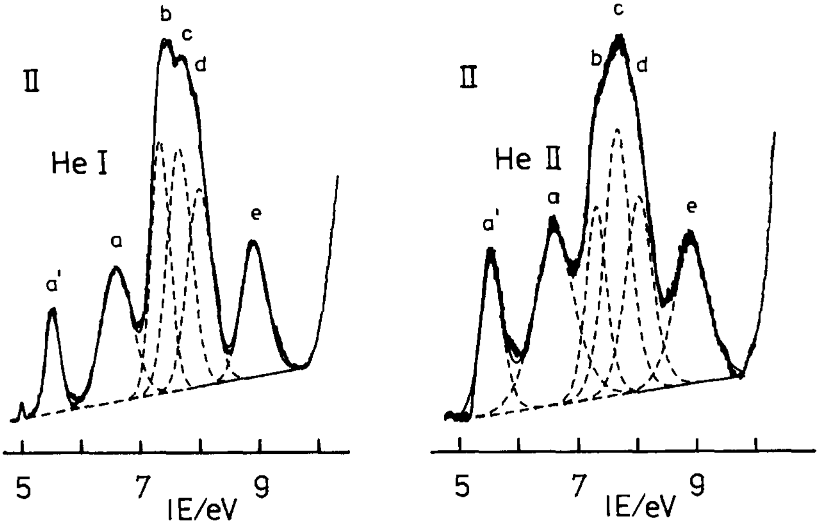


Fig. 3. HeI and HeII PE spectra of Cp*Fv*Ti (II).

group amounts to 0.25 eV for Cp'_2TiCl_2 complexes [13]. Thus with respect to the value 8.07 eV for IV, values 7.8 and 7.6 eV can be expected for the tetra- and the penta-methylated cyclopentadienyl ligand. The band maxima of 7.79 and 7.63 eV for Ia and Ib, respectively, are close to those values. The σ(Ti–CH_3) *IE* is ca. 0.3 eV lower than the vertical *IE* for the cyclopentadienyl-based ionizations in IV. The intensity ratio **c**/**a** indicates that more than two ionization events may fall within the strong band **c**. Thus the σ(Ti–CH_3) ionization can contribute to the intensity of band **c**. The remaining band **d** can be thus assigned to the fulvene-localized π-orbital (27 MO) relating to the $2b_1$ π MO of the free ligand. The assignment of band **d** to one ionization event seems consistent with the observed **d**/**a** intensity ratio.

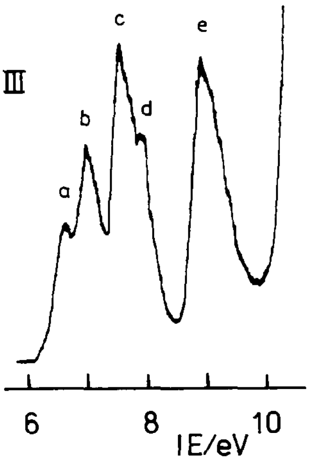


Fig. 4. HeI PE spectrum of Cp*Ad*Ti (III).

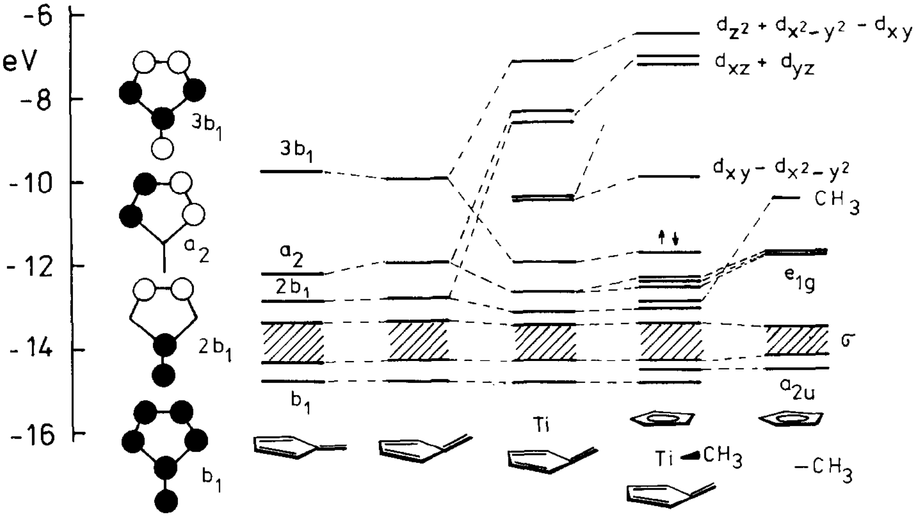


Fig. 5. Diagram of the valence orbitals of CpFvTiMe related to MOs of constitutive fragments.

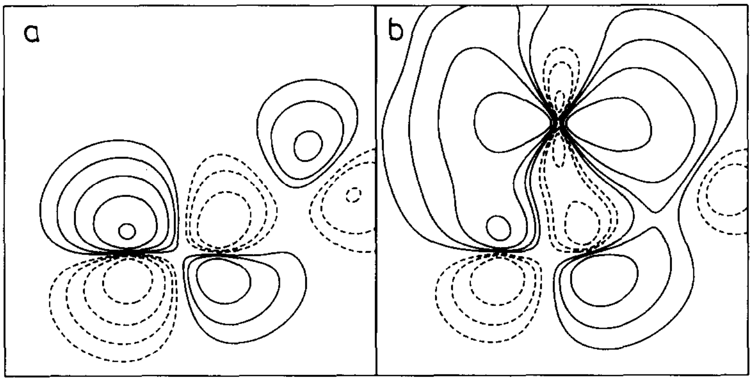


Fig. 6. Detail of the contour plots of the $3b_1$ π-MO of fulvene (a) and HOMO (32 MO) of CpFvTiMe (b) in the Ti ··· C=CH$_2$ plane. The C=CH$_2$ bond is parallel with the horizontal axis.

Table 2

Valence MOs of CpFvTiMe

MO	ϵ (eV)	% Ti	% Me	% Cp	% Fv
33 [a]	−9.96	72	4	12	12
32	−11.78	35	8	4	53
31	−12.40	8	3	41	47
30	−12.51	11	8	76	4
29	−12.65	11	7	44	38
28	−12.94	27	51	10	10
27	−13.16	15	–	3	82
⋮					
18	−14.59	4	–	63	33
17	−14.95	–	–	35	65

[a] Lowest unoccupied MO (LUMO).

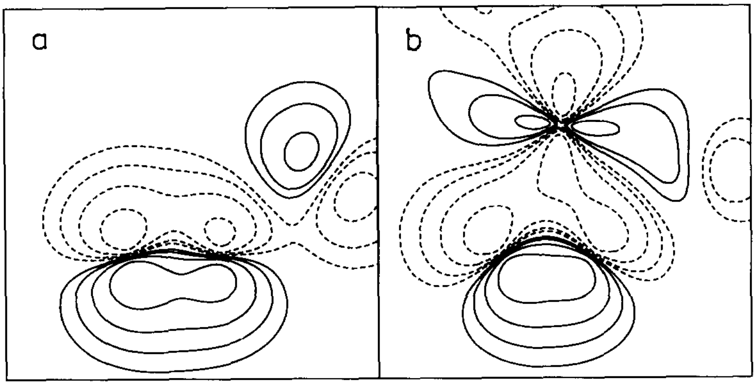


Fig. 7. Detail of the contour plots of the $2b_1$ π-MO of fulvene (a) and 27 MO of CpFvTiMe (b) in the Ti · · · C=CH$_2$ plane.

*Cp*Fv*Ti (II)*

A new low energy band at 5.54 eV (**a**′) is present in the PE spectrum of II when compared with that of Ia. The shapes of bands **a**–**e** are very similar in both spectra, and the band positions differ less than by 0.15 eV (Fig. 3). The He(II)/He(I) intensity ratios and band intensities obtained by decomposition into six Gauss–Lorentz product functions are summarized in Table 3. Band **a**′ becomes more intense in the He(II) spectrum relative to bands **b**–**e** and so this band is assigned to the metal-based *d*-electron ionization. According to the EHT MO scheme the singly occupied HOMO (19*a*′) has an 80% contribution from the Ti *d*-orbitals (Table 4). The relative decrease in the intensity of the band **a** is slightly lower than that of bands **b**–**e**. According to the EHT calculation a strong interaction between the $3b_1(\pi)$ orbital of fulvene and central atom *d*-orbitals is to be expected (Fig. 8).

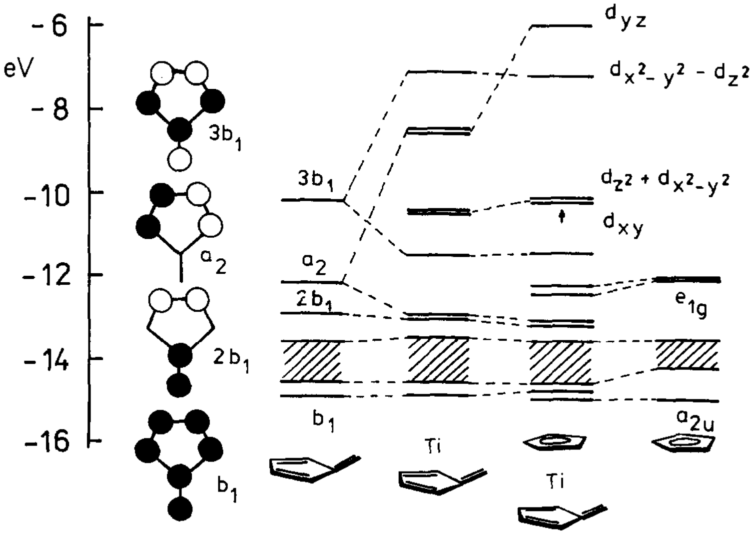


Fig. 8. Diagram of the valence orbitals of CpFvTi related to MOs of constitutive fragments.

Table 3

He(II)/He(I) relative band intensities in the PE spectra of Cp*Fv*Ti (II)

Band	Intensity (a.u.)		
	HeI	HeII	HeII/HeI
a′	1.0	1.0	1.00
a	2.8	2.0	0.71
b	3.2	1.2	0.38
c	4.0	2.1	0.53
d	3.4	1.6	0.47
e	2.4	1.5	0.63

Although the 1 : 1 mixing is an overestimate, the observed intensity changes indicate a larger *d*-orbital contribution than for bands **b**–**e**. Thus band **a** is assigned to the 18*a*′ MO correlated with the fulvene $3b_1(\pi)$ orbital. Three ionizations are found within the intense feature between 7 and 8.5 eV. In the light of the MO calculation and the assignment of the spectra of Ia and Ib, bands **b**–**d** are assigned to the predominantly cyclopentadienyl-based ionizations. The EHT calculation indicates that the following 10*a*″ and 15*a*′ MOs are very close in energy. The symmetric shape of the band **e** and the **e**/**a** intensity ratio indicate that band **e** comes from one rather than two ionization events. Thus band **e** is assigned to 15*a*′ MO correlated with the fulvene $2b_1(\pi)$ orbital, and the 10*a*″ MO having the predominant fulvene $a_2(\pi)$ character is assigned to the overlapping bands **b**–**d**. The contour maps in the Ti ··· C=CH$_2$ plane for 18*a*′ and 15*a*′ MOs are similar to those for the CpFvTiMe complex, and indicate π-coordination of the exomethylene group to the central atom.

The MO analysis indicates that the LUMO has predominantly d_{z^2} character (z axis perpendicular to the ring plane). An 80% contribution to SOMO comes from the d_{xy} orbital. The fulvene $a_2(\pi)$ and $2b_1(\pi)$ orbitals are stabilized by the interaction with the d_{xz} and d_{yz} orbitals (the e_1 symmetry species in the C_{5v} symmetry). A significant difference between the η^6-coordination of fulvene and

Table 4

Valence MOs of CpFvTi

MO	C_s	ϵ (eV)	% Ti	% Cp	% Fv
31 [a]	19*a*′	−10.20	80	4	16
30	18*a*′	−10.39	80	9	11
29	17*a*′	−11.44	50	5	45
28	11*a*″	−12.20	3	57	40
27	16*a*′	−12.39	5	69	26
26	10*a*″	−13.05	17	30	53
25	15*a*′	−13.15	12	16	72
⋮					
16	10*a*′	−14.71	–	18	82
15	9*a*′	−14.97	–	82	18

[a] Lowest unoccupied MO (LUMO).

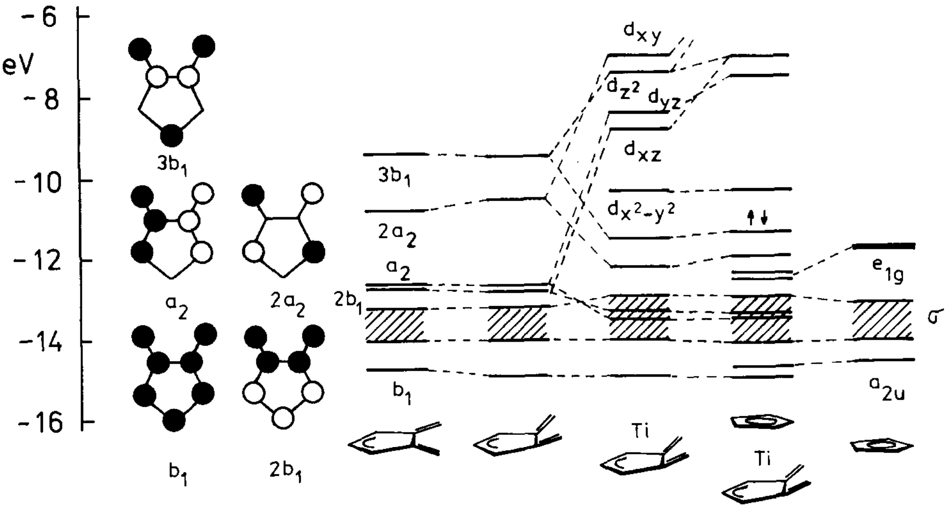


Fig. 9. Diagram of the valence orbitals of CpAdTi related to MOs of constitutive fragments.

the η^5-coordination of cyclopentadienyl lies in the stronger interaction of LUMO ($3b_1(\pi)$) of fulvene with the d orbitals owing to the smaller $3b_1(\pi) - d$ energy gap compared with the energy difference $e_1(\pi) - d$ and $e_2(\pi) - d$ for the cyclopentadienyl ligand.

*Cp*Ad*Ti (III)*

Five transitions are resolved in the low IE region of the PE spectrum (Fig. 4). The MO scheme can be built up analogously from the π MOs of the allyldiene and cyclopentadienyl species and titanium d orbitals. The interaction of the d orbitals with the allyldiene π orbitals strongly stabilizes the $3b_1(\pi)$ and the $2a_2(\pi)$ orbital (Fig. 9). The d_{z^2} and d_{xy} orbitals are predominantly involved in this interaction (xz is the plane of symmetry and the z axis is perpendicular to the ring plane). The weaker stabilization of the $a_2(\pi)$ and the $2b_1(\pi)$ orbital is brought about by the overlap with d_{yz}, d_{xz} and d_{xy} orbitals. The contour plots of these

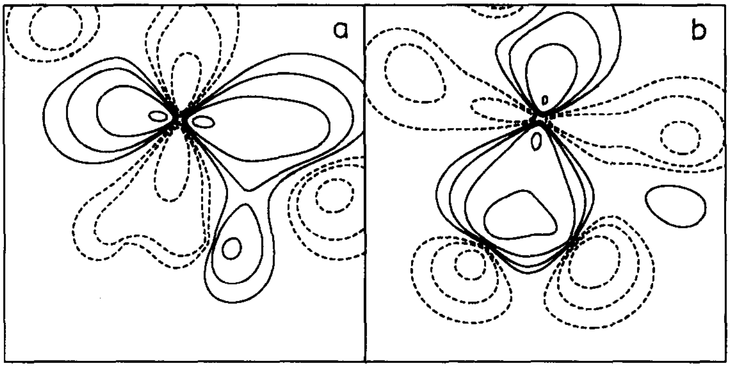


Fig. 10. Detail of the contour plots of HOMO ($18a'$) (a) and $13a''$ MO (b) of CpAdTi in the Ti$\cdots$C=CH$_2$ plane.

Table 5

Valence MOs of CpAdTi

MO	C_s	ϵ (eV)	% Ti	% Cp	% Ad
30 [a]	17*a*′	−10.41	80	9	11
31	18*a*′	−11.45	38	3	57
30	13*a*″	−12.03	25	21	54
29	17*a*′	−12.48	17	62	21
28	12*a*″	−12.61	9	77	14
27	11*a*″	−13.06	4	6	89
26	16*a*′	−13.18	4	4	92
25	15*a*′	−13.36	7	8	85
24	10*a*″	−13.54	8	17	75
⋮					
17	12*a*′	−14.83	–	57	43
16	11*a*′	−15.05	–	41	59

[a] Lowest unoccupied MO (LUMO).

MOs in the Ti ··· CH_2=C plane indicate that the π-character of the methylene groups is retained (Fig. 10). In the light of the EHT results the bands **a** and **b** in the PE spectrum can be assigned to the 18*a*′ and 13*a*″ MOs related to the $3b_1(\pi)$ and $2a_2(\pi)$ orbitals of the allyldiene ligand, respectively. The contributions of the *d* orbitals in these levels amount to 38 and 25%, respectively (Table 5). The third and fourth occupied MOs (17*a*′, 12*a*″) are mainly localized on the cyclopentadienyl ligand. Band **c**, with the high energy side shoulder **d**, may come from the cyclopentadienyl-based ionizations. The *IE*s 7.52 and 7.84 eV are close to those for Ia. The calculation places the 15*a*′ and 10*a*″ MOs related to the allyldiene $a_2(\pi)$ and $2b_1(\pi)$ orbitals below two highest σ levels. This seems to be the result of the EHT underestimation of the $\sigma - \pi$ gap. The band **e** peaking at 8.91 eV is tentatively assigned to the $a_2(\pi)$ and $2b_1(\pi)$ allyldiene orbitals.

Conclusion

The PE spectra of the fulvene–titanium and the allyldiene–titanium complexes have been interpreted on the basis of comparisons and of the fragment MO scheme based on the extended Hückel formalism. The MO analysis indicates that the exomethylene groups in the fulvene and allyldiene ligands are π-coordinated to the central atom. The complexes Cp*Fv*TiMe and $(Me_4Cp)(Me_3Fv)TiMe$ may be regarded as d^0 species but their HOMOs have considerable metal *d*-orbital contribution. The SOMO in Cp*Fv*Ti is localized predominantly on the transition metal center and the complex has formally a d^1 configuration. This implies that the Fv* ligand is a formal dianion in these complexes, which is understandable in view of the double occupancy of the fulvene $3b_1(\pi)$ orbital. The allyldiene complex is likewise a d^0 species, for which, however, the strong mixing of the ligand $3b_1(\pi)$ and $2a_2(\pi)$ orbitals with the central atom *d* orbitals makes trivial electron counting, which results in the −3 charge of the allyldiene ligand, highly formal. This assignment is supported by the electronic absorption spectra: the presence of only one absorption band in the visible and near infrared region (550–605 nm

[18,25]) is not expected for d^2 and d^3 complexes, and the molar extinction coefficients of these bands ($\epsilon \geq 200$ cm^2 mmol^{-1}) are consistent with a π–d nature of the electronic absorptions. The agreement between the spectra with the results of the MO calculations confirms the validity of the EHT results.

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