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Electronic structure of bis-cyclopentadienyl-titanium dihalides as indicated by UV photoelectron spectroscopy

Tomáš Vondrák, Karel Mach and Vojtech Varga

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 182 23 Prague 8 (Czechoslovakia)

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Abstract

The He(I) photoelectron spectra have been obtained for a series of bis(η^5-cyclopentadienyl)titanium dihalide complexes $(C_5H_{5-n}(CH_3)_n)_2TiCl_2$ ($n = 0, 1, 3, 4, 5$) and $(C_5H_{5-n}(CH_3)_n)_2TiBr_2$ ($n = 0, 1, 3$). From the progressive displacements of the photoionization bands upon methylation it follows that the cyclopentadienyl π-orbitals are ionized at lower energies than halogen lone pairs. The cyclopentadienyl $a_1 + b_1$ symmetry species lie above the $a_2 + b_2$ ones. The dichloride and dibromide complexes do not differ in the extent of interaction between halogen p orbitals and cyclopentadienyl π-orbitals.

Introduction

The rich chemistry of bent metallocene complexes [1,2] stimulated an extensive investigation of their electronic structures. The qualitative bonding scheme for the bent bis-cyclopentadienyl-metal species was developed by Green et al. [3], and the quantitative aspects of this bonding model were investigated by the extended Hückel method [4]. Ultraviolet photoelectron (PE) spectroscopy is a potent tool for the determination of the energetics of ion states which can be expressed in terms of one-electron energies [5]. The PE spectra of bis(η^5-cyclopentadienyl)metal dihalides of group IVB have been described by several authors [6,7,8]. Differences in the earlier papers were conclusively analysed by Cauletti et al. [8] on the basis of He(I)/He(II) intensity ratios. The values of the He(I)/He(II) intensity ratio led to the assignment of the chlorine p-orbitals to higher ionization energies and the cyclopentadienyl π orbitals to lower ones. This order was found to be reversed in cp_2TiI_2 (cp = cyclopentadienyl), and no clearcut conclusion could be drawn from the PE spectrum of cp_2TiBr_2. On the basis of these results a bonding model involving an extensive mixing of bromine p orbitals and cyclopentadienyl π-orbitals was postulated [8]. INDO calculations suggest that this interaction is stronger in the

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dichloride than in the dibromide species [9]. SCF-X-α-SW calculations support the above assignment of the PE spectrum of cp_2TiCl_2 [10]. The applicability of the Koopmans' theorem seems justified by these calculations.

The methylation of the cyclopentadienyl ligand provides a valuable information for the assignment of PE bands. The ionizations localised on the cyclopentadienyl ligand show a larger shift than those localized on the central atom or other ligands [11]. In terms of simple molecular orbital concepts the displacements of bands upon methylation are proportional to the square of atomic orbital coefficients at the point of substitution [12]. This straightforward interpretation of the shifts of ionization energies (IE's) is complicated by a contribution due to the coulombic effect of substituent. In a series of ferrocene derivatives the shifts of metal-based ionizations are much larger than would be inferred from the delocalization of *d* orbitals [13]. Thus relative IE shifts within a series of compounds differing in the degree of methylation and in structuraly related systems indicates the localization of molecular orbitals rather than absolute values of the band displacements.

We examined the He(I) PE spectra of bis(cyclopentadienyl)titanium dihalides $\overline{cp}_2TiCl_2$ and $\overline{cp}_2TiBr_2$ ($\overline{cp} = C_5H_5$ (cp), $CH_3C_5H_4$ (Mecp), 1,2,3-$(CH_3)_3C_5H_2$ (Me_3cp), $(CH_3)_4C_5H$ (Me_4cp) and $(CH_3)_5C_5$ (Me_5cp) for the dichlorides, and $\overline{cp}$ = cp, Mecp, and Me_3cp for the dibromides) with the aim of gaining a deeper insight into the character of the outermost occupied molecular orbitals, and to reexamine the extent of the orbital interactions deduced from the He(I)/He(II) intensity ratios [8] and calculated within the semiempirical INDO formalism [9].

Experimental

The $\overline{cp}_2TiCl_2$ complexes were prepared under argon by published methods [14]. The same procedures were used for the preparation of the dibromides. The purity of each sample was checked by mass spectrometry.

The He(I) PE spectra were recorded on the VG Scientific UVG 3 instrument. An adequate signal to noise ratio was attained in the temperature range 190–220 °C. Ar and Xe were used as internal calibrants. The electron analyser was operated in the constant passing energy mode with a working resolution (FWHM) of 30–40 meV.

Calculations on the cp_2Ti fragment were carried out by use of the parameters adopted by Hoffmann and Lauher [4].

Results and discussion

The PE spectra of the titanocene dihalides are discussed in terms of the MO model [3]. The MO scheme (Fig. 1) is based on the interaction of group orbitals of the bent bis-cyclopentadienyl metal fragment with the *p* orbitals of halogen atoms. The e_2', a_1', e_1'' and e_1' symmetry species of the D_{5h} cp_2Ti fragment transform as $a_1 + b_1$, a_1, $a_2 + b_2$ and $a_1 + b_1$, respectively, in the C_{2v} group. The energy of the halogen *p* orbitals estimated from the overlap is $1a_1 < 2a_1 < 1b_2 < 1a_2 < 1b_1 < 2b_1$ (Fig. 1). The $2a_1$ and $1b_1$ orbitals are involved in the Ti–X σ-bonding, and this interaction brings them below the $p(\pi)$-halogen orbitals.

$\overline{cp}_2TiCl_2$ complexes

The PE spectrum of cp_2TiCl_2 can be divided into two principal parts (Fig. 2). In the region above 12 eV ionizations of cyclopentadienyl σ-orbitals, $a_1(\pi)$ and a_2 (π)

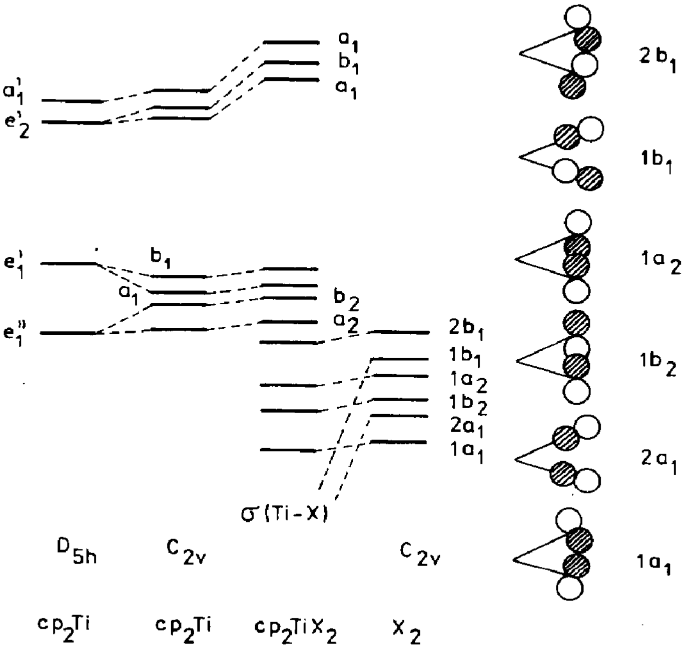

Fig. 1. Interaction scheme for cp_2TiX_2.

level and σ(Ti–Cl) orbitals give rise to broad unresolved bands. Bands below 12 eV come from the $e_1(\pi)$ localized levels of the cp ligand and halogen $p(\pi)$ orbitals not involved in the Ti–Cl σ-bonding. The vertical IE's are in reasonable agreement with earlier data [8]. Replacement of the cp ligand by Mecp brings about a general decrease in the IE's (Table 1). The IE's of the first three bands (*a–c*) are lower by 0.21–0.26 eV. The band (*d*) shows the highest sensitivity to the methylation (ΔIE 0.44 eV), and a well-resolved band is observed in the PE spectrum instead of a shoulder in the spectrum of cp_2TiCl_2. The ionizations (*e–g*) are lowered in energy by 0.13–0.22 eV.

The introduction of three Me groups into the cp ligand leads to a change in the overall appearance of the PE spectrum. With the increase in the number of methyl groups the onset of σ-ionizations is shifted to a lower IE and becomes superimposed on bands *e* to *g*. The shape of the ionzations (*a–c*) differs from the parent compound. The ionization (*c*) seems to undergo a higher shift than (*b*) upon methyl substitution, and ionizations (*b*) and (*c*) coalesce into one band. The lowering of the energy of the ionizations (*a–d*) with respect to cp_2TiCl_2 amounts to 0.61–1.11 eV. The bands *c* and *d* show the largest shift, of 0.82 and 1.11 eV, respectively. The bands *e–g* are shifted by 0.37–0.63 eV, and a shoulder (*f'*) appears which has no counterpart in the spectra of the cyclopentadienyl and methylcyclopentadienyl species.

The $(Me_4cp)_2TiCl_2$ ionizations (*a–c*) undergo a further low IE shift, while the features *e–g* are practically insensitive to the introduction of the fourth methyl group. The average destabilization per methyl group in $(Me_4cp)_2TiCl_2$ is 0.20, 0.22, 0.27, and 0.32 eV for bands *a–d*, respectively. The sensitivities of bands *e–g* are lower (0.17, 0.10 and 0.11 eV, respectively). The larger effect of methylation on features *a–d* indicates that they originate in the cyclopentadienyl-based ionizations.

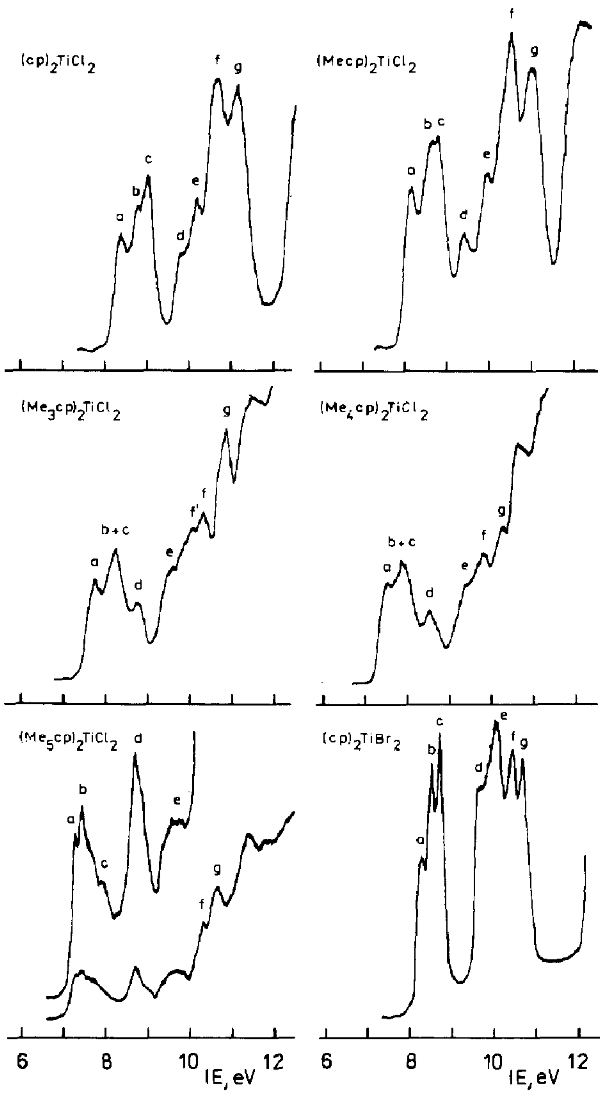

Fig. 2. He(I) photoelectron spectra of cp_2TiCl_2, $(Mecp)_2TiCl_2$, $(Me_3cp)_2TiCl_2$, $(Me_4cp)_2TiCl_2$, $(Me_5cp)_2TiCl_2$ and cp_2TiBr_2.

This agrees with the assignment based on the He(I)/He(II) intensity ratio [8]. The average lowering of the energy of the ring π-ionizations by 0.25 eV per one methyl group is larger than that observed at $cpTiX_3$ half-sandwich complexes [15].

The IE's of the cyclopentadienyl π-levels in $(Me_5cp)_2TiCl_2$ do not seem consistent with the almost additive destabilization per methyl group observed up to to the Me_4cp species. Bands *a* and *b* are lowered in energy more than are the average increments per methyl group. Band *c* is lowered by 0.07 eV and band *d* is stabilized by 0.13 eV relative to $(Me_4cp)_2TiCl_2$. The steric crowding due to the methyl groups in $(Me_5cp)_2TiCl_2$ brings about an increase of the cp–Ti–cp angle to 137.4°, compared to 130.97° for cp_2TiCl_2 [16,17]. EHT calculations on the cp_2Ti fragment show that the increase of the cp–Ti–cp angle lowers the energy of the $a_1 + b_1$ π-levels, whereas the energies of the $a_2 + b_2$ π-levels are raised (Fig. 3). The band

Table 1

Vertical ionization energies (IE) of $\overline{\mathrm{cp}}_2\mathrm{TiX}_2$ (X = Cl, Br) complexes (eV)

Band	$\overline{\mathrm{cp}}_2\mathrm{TiCl}_2$, $\overline{\mathrm{cp}}$ =					Assignment	Band	$\overline{\mathrm{cp}}_2\mathrm{TiBr}_2$, $\overline{\mathrm{cp}}$ =			Assignments
	cp	Mecp	$\mathrm{Me_3cp}$	$\mathrm{Me_4cp}$	$\mathrm{Me_5cp}$			cp	Mecp IE (eV)	$\mathrm{Me_3cp}$	
a	8.40	8.15	7.74	7.60	7.29	$a_1 + b_1(\pi)$	*a*	8.29	8.10	7.74	
b	8.81	8.60	8.20 [a]	7.95 [a]	7.44		*b*	8.55	8.39	8.11	$a_1 + b_1(\pi)$
c	9.02	8.76			7.88	$a_2 + b_2(\pi)$	*c*	8.75	8.58	8.24	$a_2 + b_2(\pi)$
d	9.85	9.41	8.74	8.58	8.71		*d*	9.70	9.31	8.84	
e	10.20	9.98	9.57	9.54	9.65	p(Cl)	*e′*		9.48		p(Br)
f′			9.85	9.83			*e*	10.08	9.92	9.59	
f	10.65	10.52	10.24	10.27	10.28		*f*	10.47	10.35	10.13	
g	11.14	11.00	10.77	10.71	10.64		*g*	10.72	10.53	10.36	

[a] Overlapping bands *b* + *c*.

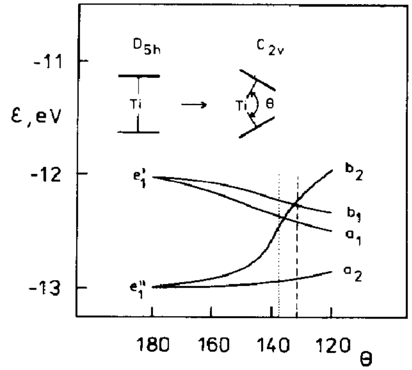

Fig. 3. Dependence of energy of ligand π-orbitals on the bending of the cp_2Ti fragment. Dashed and dotted bars denote the angle in cp_2TiCl_2 and $(Me_5cp)_2TiCl_2$, respectively.

displacements between Me_4cp and Me_5cp species are compatible with the view that the $a_1 + b_1$ lie above the $a_2 + b_2$ orbitals, and lead to the assignment of bands *a–d* given in Table 1.

Bands *e–g* are not influenced on going from the Me_4cp to the permethylated ligand. This confirms the assignment of these bands to the chlorine $p(\pi)$-orbitals, but the vertical IE's may be influenced by superposition with the increasing σ-envelope.

cp_2TiBr_2 complexes

The PE spectrum of cp_2TiBr_2 (Fig. 2) is better resolved than that described by Cauletti et al. [8]. Three sharp bands *a–c* are found instead of a single band peaking at 8.8 eV, and two bands *f* and *g* instead of a poorly resolved band at 10.5 eV. The shape of the first band system is very similar to that of the chloro derivative. The band maxima are shifted by 0.11–0.27 eV to lower IE's. Bands *e–g* are more sensitive to the replacement of chlorine by bromine, the average destabilization amounting to 0.54 eV.

When the cp ligands are replaced by Mecp ligands, the energies of *a–c* bands are lowered uniformly (within the experimental uncertainty) by 0.19 eV. Band *d*

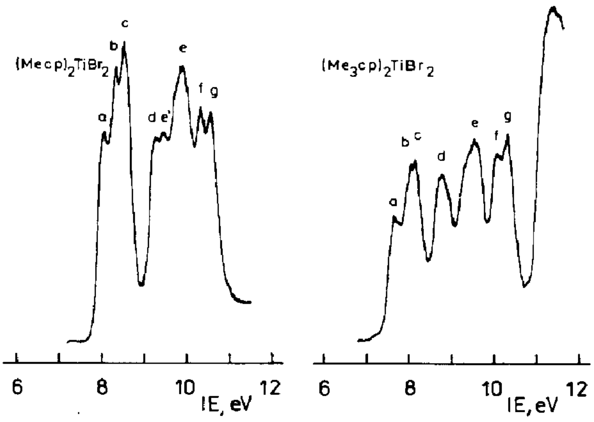

Fig. 4. He(I) photoelectron spectra of $(Mecp)_2TiBr_2$ and $(Me_3cp)_2TiBr_2$.

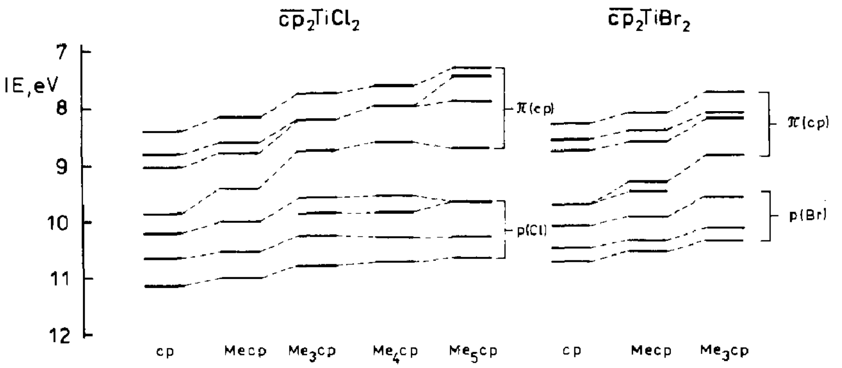

Fig. 5. Diagram of vertical ionization energies of $\overline{cp}_2TiCl_2$ and $\overline{cp}_2TiBr_2$ complexes.

exhibits the highest sensitivity to the methylation and a resolved band is found instead of a shoulder (Fig. 4).

In $(Me_3cp)_2TiBr_2$ the largest lowering of the energy of ionization of (*d*) brings about a different appearance of the spectrum. Bands *a–d* are lowered by 0.55, 0.44, 0.51 and 0.86 eV, respectively. The displacements of bands *e*, *f* and *g* amount to 0.49, 0.34 and 0.36 eV, respectively. The average displacements of bands *a–d* amount to 0.18, 0.15, 0.17, and 0.29 eV per methyl group, respectively. The average sensitivity of bands *e–g* 0.16, 0.11, and 0.12 eV per methyl, is close to that for the cp_2TiCl_2 series. The greater effect of the halogen substitution on features *e–g* and their slightly weaker response to methylation indicate that they originate in halogen-localized orbitals. The IE shift of bands (*a–d*) in $(Me_3cp)_2TiBr_2$ is 0.11–0.31 eV lower than those for the chloro derivative. Nevertheless the observed IE shifts and the shape of band system *a–d* are consistent with the assignment for the cp_2TiCl_2 series, namely to cp-based ionizations. The lower sensitivity to methylation may indicate a larger delocalization of the cyclopentadienyl π-levels in comparison to cp_2TiCl_2 (Fig. 5). The overlap of ring π-orbitals and halogen *p* orbitals depends on their direction (see Fig. 1). A larger shift of particular symmetry species would indicate an extensive delocalization over the hydrocarbon ligand. The $1a_2$ and $1b_2$ symmetry species have the most favorable orientation for overlap with ring π-orbitals. The fact that the shape of *p*(Br) ionizations is independent of the number of methyl groups and their shifts are identical with those for the $\overline{cp}_2TiCl_2$ complexes suggest the absence of any stronger interaction between a particular combination of bromine *p* orbitals and ring π-orbitals.

The He(I)/He(II) intensity ratio for chlorine *p*(π) orbitals, which is approximately 1.4 times larger than that for bromine [18,19], and the greater overlap of band *d* with halogen based ionizations may account for the difference in the He(I)/He(II) intensity ratio between cp_2TiBr_2 and cp_2TiCl_2 observed by Cauletti et al. [8].

The same sequence of occupied levels can be adopted as for cp_2TiCl_2, i.e. the cyclopentadienyl π-orbitals lie above the halogen *p* orbitals. The results of SCF calculations confirm this conclusion [10].

Conclusions

The perturbations of the electronic structure brought about by methylation have been used for a more detail assignment of the PE spectrum of cp_2TiCl_2. The additivity of the effect of methylation on the ionization energies does not extend to the permenthylated species, apparently due to a change in the cp–Ti–cp angle resulting from steric hindrance. The effects of ligand methylation do not confirm the previously suggested difference between bonding models for cp_2TiBr_2 and for cp_2TiCl_2. The same sequence of occupied levels and the MO scheme apply to bis-cyclopentadienyl-titanium dichlorides and dibromides.

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