MOLECULAR ORBITALS AND PHOTOELECTRON SPECTRA OF SOME TITANIUM(IV) ORGANOMETALLIC COMPOUNDS

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(Received March 7th, 1977)

Summary

The photoelectron spectra of some titanium(IV) organometallic compounds are reported, and the data and the bonding in the compounds are discussed with the aid of extended CNDO/2 calculations.

Introduction

Interest in the titanium compounds $TiR_{4-x}X_x$ (R = Me, X = Cl, OR, NR_2, Cp) lies mainly in the nature of the titanium—carbon bond which is thought to be one of the major influences on the mechanism of olefin polymerisation [1,2].

Photoelectron spectroscopy is a most appropriate technique for the determination of the energy levels of molecular orbitals. However, assignment of the spectra, and particularly in this case the assignment of the Ti—C bond ionization potentials, often requires quantum mechanical calculations. The extended CNDO/2 method [3] has proved very useful as a semi empirical method for comparative purposes in series of large transition metal compounds [4—7].

This paper reports the photoelectron spectra of $TiMeCl_3$, $TiMe(OR)_3$, Ti-$(OMe)(OR)_3$, $TiMeCp(OR)_2$, $TiMe(NR_2)_3$ and $TiCpCl_3$. The tentative assignments of these spectra have been based on extended CNDO/2 calculations, which provide some insight into the bonding.

Experimental and computation

$TiMeCl_3$ was prepared by reaction of $AlMe_3$ with $TiCl_4$ in hexadecane [8] and was separated by sublimation as purple crystals. $TiMe(O-i-Pr)_3$ was prepared by the reaction of MeLi on $TiCl(O-i-Pr)_3$ in ether and purified by distillation [9], $Ti(OMe)(O-i-Pr)_3$ by bubbling oxygen through a solution of $TiMe(O-i-Pr)_3$ in CCl_4 and $TiMeCp(O-i-Pr)_2$ by reaction of MeMgI with $TiCp(O-i-Pr)_3$ in ether fol-

lowed by distillation [10]. $TiCpCl_3$ was prepared by treating $TiCp(OR)_3$ with an excess of CH_3COCl in CCl_4 and isolated by filtration as orange crystals [11]. A sample of $TiMe(NEt)_3$ was kindly supplied by R. Choukroun [12].

^{1}H NMR spectra and elemental analyses (Ti, Cl, C, H) confirmed the purity of the compounds.

The He(II) photoelectron spectra were recorded using a Perkin—Elmer Model PS 18 spectrometer. The spectra were calibrated by introducing argon or krypton into the ionization chamber before and after the measurement of the compound. The ionization potentials (IP) measurements had a precision of ±0.05 eV.

The energy levels distribution and electronic structure of the studied molecules were calculated by the extended CNDO/2 method [3]. The values of the $4s$, $4p$ and $3d$ orbital-exponents α and β parameters of the titanium atom were fitted [13] to the results of ab initio calculations of the energy levels distribution and electronic structure of $TiCl_4$ [14] and TiH_3F [15], and to the photoelectron spectra of $TiCl_4$ [16]. The optimized values used are: $\alpha_{4s} = 1.26$, $\beta_{4s} = -12.0$, $\alpha_{4p} = 0.375$, $\beta_{4p} = -10.0$, $\alpha_{3d} = 2.24$, $\beta_{3d} = -19.0$. They are consistent with those previously published for Ni, Fe, Cr [4]. Moreover, except for the $4p$ orbital parameters, they are in good agreement with those proposed by Clack et al. [17] and Chailler et al. [18].

Results and discussion

TiMeCl₃

The photoelectron spectrum of $TiMeCl_3$ is shown in Fig. 1. There are striking similarities between the spectra of $TiMeCl_3$ and $TiCl_4$ [16]. The bands at 11.7, 12.7, ~13.5 and 13.9 eV, which probably correspond to energy levels mainly composed of Cl orbitals as in $TiCl_4$ [13,14], show the same pattern and identical IP values in both spectra. The additional weaker band at 10.8 eV in

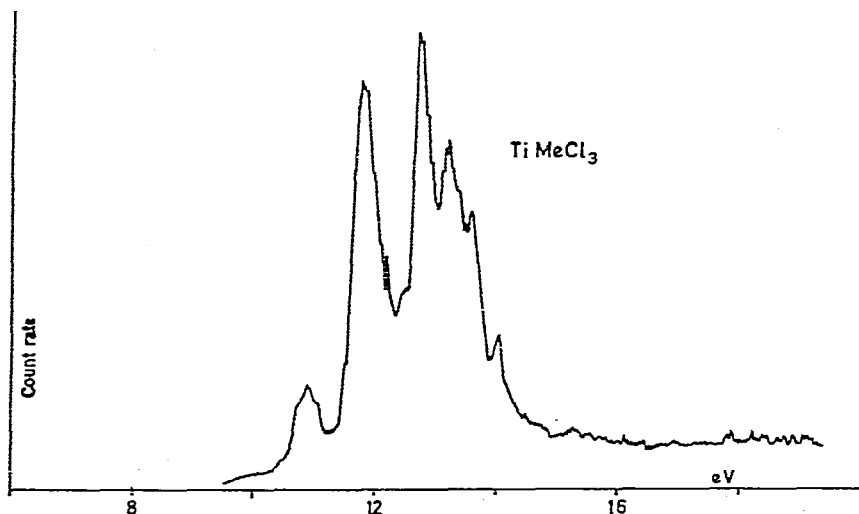Fig. 1. The photoelectron spectrum of TiMeCl₃.

the spectrum of $TiMeCl_3$ can reasonably be assigned to a Ti—C level of symmetry a_1. Since the geometrical structure of $TiMeCl_3$ is not experimentally known, the quantum calculations were carried out on a partially optimized geometrical model, tetrahedral angles being assumed throughout. It should be noted that the optimized (Ti—C) bond length is 2.15 Å, which is identical to the experimental value in tetrabenzyltitanium [19]. The Ti—Cl bond length was taken as 2.17 Å, as in $TiCl_4$ [20], and the C—H bond length as 1.10 Å.

The computed molecular orbitals levels, i.e. the theoretical IP values within Koopmans' approximation, for $TiMeCl_3$ are listed in Table 1 and characterized by C_{3v} point group symmetry. Calculated eigenvalues are expected to be lower in energy and to cover a wider energy spread than the experimental values, but agreement in the ordering of the levels is generally obtained [6,7,13,21]. A tentative assignment of the experimental spectrum of $TiMeCl_3$ can be proposed: the first band at 10.8 eV (calculated IP 13.77 eV), which corresponds to the $5a_1$ level, mainly represents the titanium—carbon bond, although some mixing occurs with chlorine orbitals. This confirms our previous qualitative assignment. The second ionization potential at 11.7 eV corresponds to ionization from the $1a_2$ and $5e$ MO's (calculated IP 14.57 and 14.65 eV) which are composed of almost pure Cl p orbitals. We assign the next broad peak at ~12.7—13.9 eV to ionization from the closely spaced MO's $4e$, $4a_1$, $3e$, $3a_1$, which have a predominant Cl p character. It should be noted that this level ordering is in fairly good agreement with that predicted by Perkins et al. [6].

$TiMe(OR)_3$ and $Ti(OMe)(OR)_3$

The spectra of two of these compounds are shown in Fig. 2 and 3. The broad band at ~12—15 eV can be attributed in both cases to ionization from orbitals localized on the O-i-Pr ligands. The assignment of the three low energy bands at 9.4, 9.8 and 10.4 eV in the spectrum of $TiMe(O\text{-}i\text{-}Pr)_3$ is not obvious; the ionization from the Ti—C orbital of $TiMeCl_3$ has been previously found at 10.8 eV and the oxygen $2p$ orbitals ionizations are known to fall in the 9—11 eV range [22]. Moreover the modification of the intensity pattern of the corresponding bands of $Ti(OMe)(O\text{-}i\text{-}Pr)_3$ at 9.1, 10.0 and 10.5 eV could be related to the absence of any Ti—C bond in the latter molecule. However such an empirical assignment looks uncertain and must be supported by quantum calculations.

TABLE 1

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (eV) OF $TiMeCl_3$

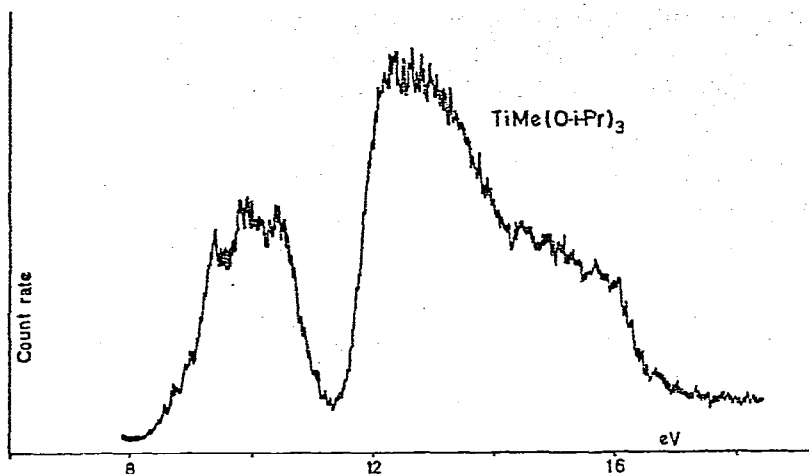| Experimental	Symmetry (C_{3v})	Calculated	Orbital character
10.8	$5a_1$	13.77	Ti—C
11.7	$\lceil 1a_2$	14.57	Cl
	$\lfloor 5e$	14.65	Cl
12.7	$\lceil 4e$	15.46	Cl
13.1	$4a_1$	15.75	Cl + Ti
13.5	$3e$	16.16	Cl + Ti
13.9	$\lfloor 3a_1$	16.35	Cl

Fig. 2. The photoelectron spectrum of TiMe(O-i-Pr)₃.

In order to reduce computing time, the calculations have been carried out on TiMe(OMe)$_3$ and Ti(OMe)$_4$ instead of the O-i-Pr derivatives. The following geometrical parameters were assumed: d(Ti—C) 2.15 Å; d(Ti—O) 2.0 Å; d(C—O) 1.43 Å; d(C—H) 1.10 Å; tetrahedral and trigonal environment have been taken for the titanium and oxygen atoms respectively. Theoretical conformational analysis was carried out for both molecules: in TiMe(OMe)$_3$ the methyl group linked to the titanium is found staggered with respect to the (Ti—O) bonds, and the OMe groups are rotated by a dihedral angle (θ) of 100° around the Ti—O bond ($\theta = 0°$ when the C—O bonds are eclipsing the Ti—C bond); in Ti(OMe)$_4$ the preferred conformation is found at $\phi = 60°$ for all OMe groups (ϕ is now the dihedral angle between the OTiO and TiOC planes). The energy levels for these preferred conformations are shown in Table 2.

As expected, the high energy IPs (>12 eV) correspond in both spectra to ionization from orbitals of the (OR) ligands. In TiMe(OR)$_3$ the orbitals which
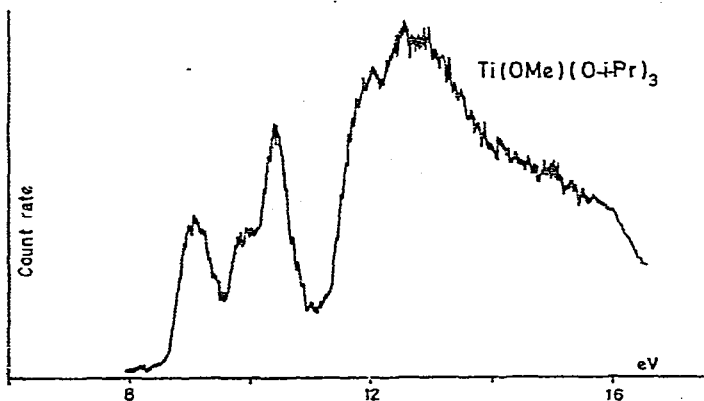

Fig. 3. The photoelectron spectrum of Ti(OMe)(O-i-Pr)₃.

TABLE 2

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (eV) OF TiMe(OR)$_3$ AND Ti(OMe)(OR)$_3$

TiMe(OR)$_3$				Ti(OMe)(OR)$_3$			
Exp. (R = i-Pr)	Sym. (C_{3v})	Calcd. (R = Me)	Orbital character	Exp. (R = i-Pr)	Sym. (S_4) [a]	Calcd. (R = Me)	Orbital character
9.4	9a$_1$	12.73	Ti + O	9.1	7a	12.64	Ti + O
9.8	⌠ 8e	13.62	Ti + O	shoulder	⌠ 7b	13.46	Ti + O
	⌡ 8a$_1$	13.80	(Ti—C) + O	at ~10	⌡ 7c	13.75	Ti + O
10.4	⌠ 7e	14.39	O(2p)		⌠ 6c	14.56	Ti + O
	⌡ 7a$_1$	14.80	Ti—C + O	10.5	{ 6a	·14.64	O(2p)
					⌡ 6b	14.86	Ti + O
Broad	⌠ 6a$_1$	17.90	C—O	broad	⌠ 5e	18.03	(C—O)
band	⌡ 6e	18.04	C—O	band	⌡ 5a	18.15	(C—O)
12—15		.	.	12—15	{ 5b	18.50	Ti + O + C
	⌡ .	.			⌡ .	.	
	.	.			.	.	
	.	.			.	.	

[a] Symmetry for the Ti(OMe)$_4$ model.

mainly figure in the titanium—carbon bond are the 8a$_1$ and 7a$_1$ MOs * and contribute respectively to the second (9.8 eV) and the third (10.4 eV) bands, together with MOs composed of titanium and oxygen orbitals. When going from TiMe(OR)$_3$ to Ti(OR)$_4$, these Ti—C MOs are replaced by additional MOs composed of Ti and O orbitals. The modification in the intensity pattern of the low energy bands is not due, as previously suggested, to the absence of Ti—C IPs which would reduce the intensity of the second and third peaks, but rather to the contribution of an additional MO to the third band.

TiMeCp(OR)$_2$

The spectrum of the compound with R = Et is shown in Fig. 4. As in the spectrum of TiMe(O-i-Pr)$_3$, two main groups of bands are observed, a broad band at 12—14 eV which can, as previously, be mainly attributed to ionization from orbitals localized on the (OR) ligands, and a group of two low energy bands at 8.7 and ~10.2 eV; given the energy of these two bands, they probably result from ionization of 2p oxygen orbitals, of one or more Ti—C MOs and of Cp ring MOs [23].

This intuitive assignment is confirmed and the content of the bands is specified by the results of the calculations. Identical geometrical parameters values to those used for TiMe(OMe)$_3$ were taken for TiMeCp(OMe)$_2$. The other parameters relative to the Cp rings were those which have been measured for TiCpCl$_3$ [24]. In the calculated preferred conformation, the Cp ring was found freely

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* This result is not surprising as molecular orbital theory applies to a model delocalized over the whole basis of the atomic orbitals. Only rarely can one bond be correlated, as in TiMeCl$_3$, to one unique molecular level.
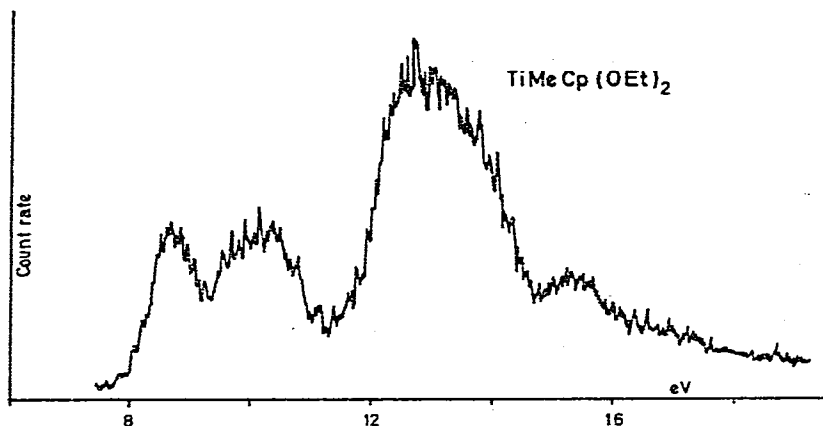
Fig. 4. The photoelectron spectrum of TiMeCp(OEt)$_2$.

rotating, the CH$_3$ group staggered with respect to the Ti—O bonds, and the two OMe groups eclipsing the Ti—C bond.

As shown in Table 3, the first band centered at 8.7 eV corresponds to ionization from MOs mainly composed of oxygen and Cp-ring orbitals. These orbitals are also present in the three levels to which the second band at 10.2 eV is assigned, but the 16a' and 15a' levels mainly represent the Ti—C bond. The broad band at 12—14 eV corresponds not only, as expected, to OR ligand orbitals but also to C(Cp)—H bond orbitals.

TiMe(NR$_2$)$_3$

The spectrum of TiMe(NEt$_2$)$_3$ is shown in Fig. 5. The experimental and calculated ionization potentials are listed in Table 4. The following geometrical parameters for the calculation of the energy level distribution of a TiMe(NMe$_2$)$_3$ model, were assumed: d(Ti—C) 2.15 Å; d(Ti—N) 2.2 Å [25]; d(N—C) 1.47 Å [26]; d(C—H) 1.10 Å. Tetrahedral environment was taken for the titanium and

TABLE 3

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (eV) OF TiMeCp(OR)$_2$

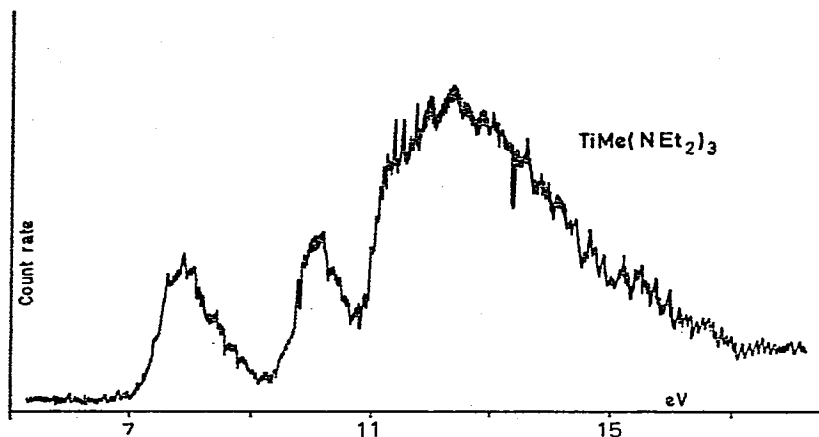| Experimental	Symmetry C_s	Calculated	Orbital character
8.7	13a″	12.53	Ti + Cp + O
	18a′	12.55	Ti + Cp + O
	17a′	12.98	Ti + Cp + O
	12a″	13.34	Ti + Cp
10.2	16a′	14.27	(Ti—C) + O
	15a′	14.45	(Ti—C) + Cp + O
	11a″	14.65	Ti + Cp + O
12—14	14a′	16.98	C(Cp)—H
	10a″	17.00	C(Cp)—H
	13a′	17.34	C(Cp)—H
	9a″	17.36	C(Cp)—H
	12a′	17.56	(C—O)
	8a″	17.75	(C—O)

Fig. 5. The photoelectron spectrum of TiMe(NEt₂)₃.

nitrogen atoms. In the calculated preferred conformation, one N—C bond of each NMe_2 group is eclipsing the Ti—C bond.

The first low energy band at 7.6 eV corresponds as expected [22] to ionization from nitrogen $2p$ orbitals, and the broad band at 12.1 eV to ionization from orbitals of the NR_2 groups. The orbitals which figure mainly in the titanium—carbon bond are the $10a$ and $11a$ MOs and contribute to the intermediate band observed at 10.1 eV.

$TiCpCl_3$ versus $TiCp_2Cl_2$

The spectrum of $TiCpCl_3$ is shown in Fig. 6. The experimental and calculated ionization potentials are listed in Table 5. The calculations were performed using the geometrical structure determined by X-ray crystallography [24].

As can be expected from the comparison with the average ionization energy of the $3p$ chlorine orbitals, the bands at 10.7, 11.4 and ~12.1 eV can be attributed to ionizations from MOs mainly composed of chlorine orbitals with some mixing with Cp orbitals in the $6e$ levels. These bands are shifted by $\simeq 1$ eV to low energy with respect to the corresponding bands of $TiCl_4$ [16]. This shift can be related to the replacement of a chlorine atom by a cyclopentadienyl

TABLE 4

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (eV) OF TiMe(NR₂)₃

Experimental	Symmetry C_3	Calculated	Orbital character
7.6	12a	11.03	Ti + N
	11e	11.52	Ti + N
10.1	11a	13.98	(Ti—C) + N
	10e	14.38	Ti + N + C(NR₂)
	10a	14.40	(Ti—C) + N
12.2	9e	16.17	(N—C)
	9a	16.21	(N—C)
	8e	18.84	(C—H)
	8a	18.99	(C—H)
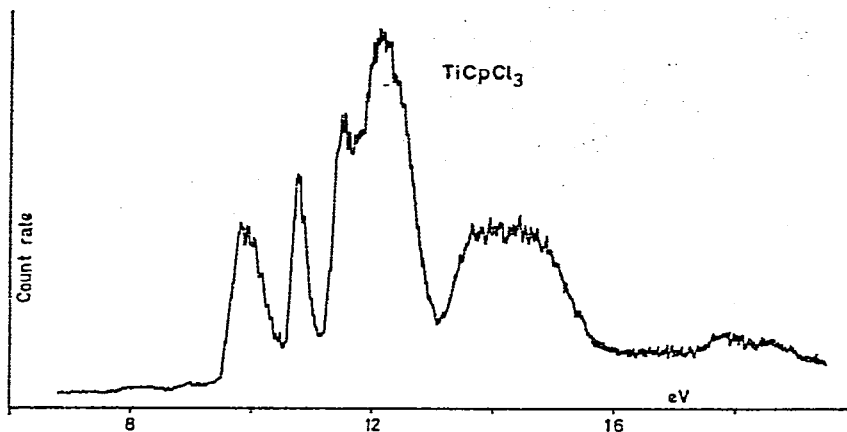
Fig. 6. The photoelectron spectrum of $TiCpCl_3$.

group, the π-donor character of which towards the d^0 metal induces a decrease of the bonding character of the chlorine lone pairs; similar interpretations have been previously reported to explain NMR measurements on alkoxytitanium derivatives [29].

The first peak at 9.8 eV (calculated 13.18 eV) corresponds to a Cp ring MO (with some mixing with chlorine orbitals) and the last broad band at 14.0 eV corresponds to the C—H bonds.

A similar pattern is found for the spectrum of $TiCp_2Cl_2$. The calculated IPs,

TABLE 5

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (eV) OF $TiCpCl_3$ AND $TiCp_2Cl_2$

$TiCpCl_3$				$TiCp_2Cl_2$				
Exp.	Sym. C_{3v}	Calcd.	Orbital character	Exp. [27]	Exp. [28]	Sym. C_{2v}	Calcd.	Orbital character
9.8	$9e$	13.18	Cp + Cl	8.45	8.46	$9b_2$	12.32	Cp + Cl
10.7	$\{^{7a_1}_{8e}$	14.32 / 14.47	Cl p / Cl p	8.90 / 9.12	(8.87) / 9.07	$8b_1$ / $6a_2$	12.95 / 13.00	Cp + Cl / Cp + Cl
11.4	$\{^{6a_1}_{5a_1}$	15.08 / 15.21	Ti + Cl / Cl	9.83	(9.95)	$7b_1$	13.82	Cl
Broad band at ~12—13	$\{^{7e}_{6e}$	15.49 / 14.21	Ti + Cl / Cl	10.22	10.24	$11a_1$ / $10a_1$	13.83 / 14.17	Cl / Cl + Cp
				10.72	10.65	$6b_1$	14.53	Ti + Cl
				11.20	11.12	$8b_2$ / $9a_1$ / $5a_2$	14.67 / 14.83 / 15.22	Ti + Cl + Cp / Ti + Cl + Cp / Ti + Cl + Cp
Broad band at ~14	$\{^{5e}_{4e}$	17.58 / 17.90	C—H / C—H		(13.11)	$7b_2$ / $5b_1$ / $4a_2$	16.49 / 17.05 / 17.12	C—H / C—H / C—H
					13.8	$8a_1$ / $6b_2$ / $3a_2$ / $4b_1$ / $7a_1$	17.23 / 17.28 / 17.45 / 17.64 / 18.18	C—H / C—H / C—H / C—H / C—H

obtained using the experimental geometry of ref. 30, are listed in Table 5 together with the experimental values [27,28]. As for $TiCpCl_3$, the spectrum of $TiCp_2Cl_2$ can be described in terms of three entities, i.e. the Cp rings (which correspond to the first bands at 8.46—9.07 eV), the MOs mainly derived from the chlorine orbitals (at 9.95—11.12 eV) and the C—H bonds (at ~13.8 eV). As previously observed when comparing $TiCl_4$ and $TiCpCl_3$, the ionization potential of the chlorine orbitals are shifted by 0.9—1 eV to low energy when passing from $TiCpCl_3$ to $TiCp_2Cl_2$. It is well known [22] that a X lone pair *IP* will decrease as X becomes less electronegative. This is reflected in this case by the decrease of the chlorine net charge; respectively — 0.33 in $TiCl_4$ [13], —0.38 in $TiCpCl_3$ and —0.43 in $TiCp_2Cl_2$. Our assignment of the spectrum of $TiCp_2Cl_2$ is in general agreement with that proposed by Dahl et al. [27] (except for the first bands, which they attribute to pure Cl $3p$ orbitals), but is different from that proposed by Tondello et al. [28].

Conclusion

The photoelectron spectra of the studied titanium(IV) organometallic compounds can be assigned with the aid of extended CNDO/2 calculations. The calculated first ionization potentials are ca. 3.5 eV lower than the experimental values but the calculated differences between the first and the second, and between the second and the third ionization potentials are in good agreement with experiment.

A decrease (~1 eV) of the ionization potential of the chlorine orbitals is observed in the series $TiCl_{4-x}Cp_x$ when one Cp group replaces one chlorine atom. This can be attributed to the π-donor character of the Cp group, which causes a decrease in the bonding character of the chlorine lone pairs.

In the methyl compounds investigated, the ionization potentials attributed to the Ti—C bond lie in the range 9.8—10.8 eV. In $TiMeCl_3$, the ionization from the Ti—C bond orbital corresponds to the first band observed in the spectrum; in the case of alkoxy and dialkylamino derivatives, however, considerable mixing occurs between the Ti—C bond orbitals and oxygen or nitrogen orbitals. Moreover two molecular orbitals at least must be taken into account for the assignment of the Ti—C energy levels, which do not correspond to the first band of the spectra. This should be kept in mind in discussions of possible correlations between catalytic activity and ionization potentials as an extension of the Cossee mechanism [2] to this type of compounds.

Acknowledgment

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