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UV Photoelectron Spectra of Some Bent Bis(η^5 -cyclopentadienyl)Niobium and Tantalum Complexes

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UV PE Spectra, Niobium and Tantalum Complexes

He(I) and He(II) photoelectron spectra are reported for (η^5 -C₅H₅)₂MLX (M = Nb, Ta; L = H, CO; X = propene, 1-butene, propyl) and some methylcyclopentadienyl derivatives. Also the spectra of some π -allyl and dihalide complexes are reported. Unambiguous assignments could be made of the metal d_{xy} orbital, the Cp orbitals, the olefin π ionization and the M-hydride and π -allyl orbitals. Very regular trends are observed in the ionization energies upon substitution of the ligands. The olefin π ionization is found at very low energy indicating that the π backbonding to the olefin is very important. He(I)/He(II) cross section differences show clearly differences in metal character of the various M.O.'s.

Introduction

In recent years much work has been done on bent bis(η^5 -cyclopentadienyl) transition metal complexes. There are several reports on the PE spectra of bis(η^5 -cyclopentadienyl) metal halide, hydride, olefin and carbonyl complexes [1-4]. M.O. calculations have also been performed on several of these complexes [5-6].

As a continuation of our work on metal olefin complexes [7] we studied the PE spectra of a series of bis(η^5 -cyclopentadienyl)niobium and tantalum hydride olefin, allyl (carbonyl), bis halide and allyl complexes. Lauer and Hoffmann [5] have done EHT calculations on these classes of complexes and have published correlation diagrams using a "molecules in molecules" approach.

For the complexes under study here the Alcock bonding model [8] is now well established. Crystallographic, EPR and UPS studies [3, 6, 9] on d⁰, d¹ and d² complexes prove that the HOMO is a metal d orbital of a₁ symmetry (in C_{2v}). Upon occupation of this orbital (going from d⁰ to d¹ to d²) the LML bond angle decreases owing to electrostatic repulsion. This upper orbital lies outside the L-M-L angle on the y axis (see Fig. 1) and is similar to a d_{yz} orbital.

Fig. 1. Structure and coordinate-system for Cp₂ML₂ type complexes.

We have interpreted the spectra of the above mentioned complexes using results from the "molecules in molecules" approach while also relying on empirical assignment criteria such as correlation with related complexes and He(I)/He(II) intensity differences [10].

Experimental

Synthesis

The compounds were prepared following published procedures.

Cp₂MCl₂ and (MeCp)₂MCl₂ (M = Nb, Ta) were made from MCl₅, CpNa (or MeCpNa) with *i*-C₃H₇MgCl as the reducing agent [11]. The hydride olefin complexes Cp₂TaH(C₃H₆), Cp₂TaH(C₄H₈) and (MeCp)₂TaH(C₄H₈) (C₄H₈ = 1-butene) were obtained from the reaction of Cp₂TaCl₂ or (MeCp)₂TaCl₂ with *n*-C₃H₇MgCl or *n*-C₄H₉MgCl [12]. Cp₂TaH(CO) was made by carbonylation of exo Cp₂TaH(C₄H₈) [13]. CpMC₃H₇(CO) and (MeCp)₂TaC₃H₇(CO) were prepared by carbonylation of the corresponding propene compounds in toluene [13]. The allyl

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compounds $\text{Cp}_2\text{MC}_3\text{H}_5$ and $(\text{MeCp})_2\text{MC}_3\text{H}_5$ were made from Cp_2MCl_2 or $(\text{MeCp})_2\text{MCl}_2$ and $\text{C}_3\text{H}_5\text{MgBr}$ in ether [14].

The paramagnetic complexes Cp_2MCl_2 and $(\text{MeCp})_2\text{MCl}_2$ were identified by elemental analysis and IR spectra. The other complexes are diamagnetic. They were identified by IR and ^1H NMR spectra and in some cases by elemental analysis.

Photoelectron spectra

The photoelectron spectra were recorded on a Perkin Elmer PS 18 spectrometer equipped with a Helectros Developments He(I)/He(II) hollow cathode source. The spectra of all complexes were obtained between 100 °C and 200 °C. Ar and Xe were used as internal calibrants. Ionization energies are accurate to 0.1 eV.

Bonding Scheme

A general bonding scheme for Cp_2ML_2 complexes has been described by various authors [5, 6] in several publications. This scheme has been used in the interpretation of PE spectra [3, 4]. Only some points of special relevance for our work will be discussed here.

The "molecules in molecules" approach starts with construction of M. O.'s for the bent Cp_2M fragment (C_{2v} symmetry when the eclipsed conformation is assumed for the Cp rings), by bending a metallocene unit. The four Cp M. O.'s constructed from the e_g orbitals of the Cp rings transform as b_1 , a_1 , b_2 and a_2 in C_{2v} symmetry. The b_2 and a_2 orbitals interact rather strongly with the metal d_{xz} (b_2) and d_{yz} (a_2) orbitals and will be more stabilized than the b_1 and a_1 orbitals which interact with metal p orbitals.

The remaining metal d orbitals $3a_1$, $2b_1$ and $4a_1$ can be used for bonding with the other ligand. The

b_1 orbital is mainly d_{yz} in character. The two a_1 orbitals each contain some contribution from the s and p_z orbitals in addition to $d_{x^2-y^2}$ and d_{z^2} contributions. The $3a_1$ orbital is directed strongly along the y axis. The $4a_1$ orbital is hybridized along the z axis away from the Cp ligands. A systematic survey of this is given by Lauer and Hoffmann. For the various classes of complexes schematic correlation diagrams are given in Fig. 2a-d. These diagrams have several features in common. Firstly, there is a π backbonding interaction between the occupied $3a_1$ metal orbital (a' in C_s symmetry), which can be described as similar to a d_{y^2} orbital, and the π^* orbitals of CO or the olefin. This stabilizes the $3a_1$ orbital. Secondly, there are the σ interactions of the ligands with the empty $2b_1$ and $4a_1$ orbitals. The relative positions of the M-ligand σ orbitals are taken from the P. E. results as will be discussed in the next section.

Results and Discussion

$\text{Cp}_2\text{NbC}_3\text{H}_7(\text{CO})$, $\text{Cp}_2\text{TaC}_3\text{H}_7(\text{CO})$ and $(\text{MeCp})_2\text{TaC}_3\text{H}_7(\text{CO})$

The spectra of these complexes are very similar in bandform and only minor shifts occur in the I. E.'s. We therefore only show the He(I) and He(II) spectra of the niobium complexes (Fig. 3). The I. E.'s are given in Table I.

In the low energy region five bands are easily observed (A-E). After these a very broad band is observed in which ionization from the ligand orbitals will occur. Band A can be very easily assigned when we compare the He(I) and He(II) spectra. This band increases significantly on going from He(I) to He(II) radiation. This indicates, together with the band

Fig. 2. Qualitative M. O. diagrams.

	Cp ₂ NbC ₃ H ₇ (CO)	Cp ₂ TaC ₃ H ₇ (CO)	(MeCp) ₂ TaC ₃ H ₇ (CO)	assignment
A	6.2	6.1	6.0	metal d (+ $\pi^*(CO)$)
B	7.7	7.9	7.8	M-C
C	8.8	8.9	8.7	Cp
D	9.4	9.5	9.3	Cp
E	10.6	10.6	10.4	C ₃ H ₇ ($\sigma(CH)$)
	(11.2)	(11.0)	(10.9)	

Table I. Ionization energies of the propyl complexes.

Fig. 3. The He I and He II PE spectra of Cp₂Nb(C₃H₇)CO.

position, that band A originates from the metal d_{z²} ionization as was described in a former section. The first I. E. of free carbon monoxide occurs at 14.01 eV [16] and is assigned to ionization of the 5 σ orbital. We can therefore assume that ionization from this ligand will all occur in the broad bands at I. E. > 13 eV. Bands B-E should originate from the propyl and the cyclopentadienyl ligands. A detailed assignment of these bands is not a priori clear. For this we need an analysis of the shifts of the I. E.'s upon methylation of the cyclopentadienyl rings and upon variation of the metal. It is clear that upon methylation the largest shifts should occur in the Cp I. E.'s. Looking at the results from the Ta complexes it is clear that the shifts are very small (<0.2 eV) and that bands C and D are the most destabilized. It can therefore be suggested that these bands originate from the Cp orbitals. More evidence for this assignment can be deduced from the shifts upon variation of the metal. It is apparent from a number of investigations [17] that variation

of the metal will affect the Cp orbital more than the other ligand orbitals. This observation leads to the conclusion that band B has more C₃H₇ character and that bands C and D should originate from the Cp rings. This is also confirmed from comparisons with related complexes in which the Cp ionization are all in the 8.8-9.6 eV range.

Having made an assignment of these bands we now take a closer look at the Cp ionizations. M. O. calculations indicate that the two most stabilized M. O.'s (1b₂ and 1a₂ in local C_{2v} symmetry) have larger metal character than the 1b₁ and 1a₁ orbitals. This can also be concluded from the P. E. spectra. On going from He(I) to He(II) bands C and D reverse in intensity indicating that band D has more metal character.

Another intensity change is observed for band E. This band almost vanishes in He(I) indicating that there is hardly any metal character in this band and probably is predominantly $\sigma(CH)$ in character. This band should originate from the propyl ligand since in for instance Cp₂MoCO no ionizations are observed in this region. We therefore assign bands B and E to ionizations from C₃H₇. Band B should then, regarding the cross section be predominantly M-C in character.

Cp₂TaH(CO)

The spectra of this complex are somewhat simpler (Fig. 4, Table II). The metal d ionization is again very easily assigned (band A). The broad band at 9.6 eV (D) with shoulders at 8.8 (B) and 9.4 (C) eV should contain ionization from the Cp rings and the M-H bonding orbital. Ionization from M-H bonding orbitals in related complexes occur invariably in this region [4]. It is difficult to give a precise position of the M-H bonding orbital, but on comparing the bandform of the Cp band in the propyl complexes with the bandform in this complex and on observing the decrease in intensity of the band at 9.6 eV in the

	Cp ₂ TaH(CO)	assignment		
A	6.3	metal d		
B	(8.8)	Cp		
C	(9.4)	Cp, M-H		
D	9.6			
	Cp ₂ TaH(C ₃ H ₆)	Cp ₂ (TaH(C ₄ H ₈))	(MeCp) ₂ TaH(C ₄ H ₈)	assignment
A	6.5	6.4	6.3	metal d (+ $\pi^*(C=C)$)
B	8.2	8.0	8.0	$\pi(C=C)$
C	9.0	8.8	8.6	Cp
D	9.5	9.4	9.2	
E	(9.6)	(9.5)	(9.4)	Cp, M-H

Table II. Ionization energies of Cp₂TaH(CO) and the olefin complexes. Fig. 4. The He I and He II PE spectra of Cp₂TaH(CO).

He (II) spectrum it can be carefully concluded that the M-H ionization occurs at 9.4-9.6 eV.

Cp₂TaH(C₃H₆), Cp₂TaH(C₄H₈) and (MeCp)₂TaH(C₄H₈) [15]

Again the spectra are rather similar and only one of them will be reproduced here (Fig. 5, Table II). Band A is again assigned to the metal d₂ orbital. Bands B-E should originate from orbitals from the olefin, the cyclopentadienyl rings and from the M-H bonding orbital. Bands C and D are similar in bandform and in position to bands B-D in Cp₂(TaH(CO)) and are therefore assigned to the Cp and M-H orbitals. Again the M-H orbital is probably contained in the high energy part of the band

Fig. 5. The He I and He II PE spectra of Cp₂Ta(C₄H₈)H.

as can be deduced from the He(I)/He(II) intensity variations. Bands B and E have no counterpart in the spectra of Cp₂TaH(CO). They must therefore be assigned to ionizations from the olefin. This is also confirmed by analysis of the shifts upon methylation of the Cp rings [17] and upon variation of the olefin. It is apparent from the He(I)/He(II) intensity differences that band B has more metal character and thus should be assigned to the coordinated $\pi(C=C)$ orbital of the olefin. When comparing the I. E. of this orbital to that of the free ligand (e.g. 8.2 eV in Cp₂TaH(C₃H₆) to 9.82 eV for propene) it is apparent that there is a large difference in electronic structure. As we have stressed before [7] such destabilizations are an indication of the importance of π backbonding in the metal-olefin band. It could be argued that another bonding scheme is required for the coordination of an olefin to this type of

Table III. Ionization energies of the allyl complexes.

	Cp ₂ Nb(C ₃ H ₅)	(MeCp) ₂ Nb(C ₃ H ₅)	Cp ₂ Ta(C ₃ H ₅)	(MeCp) ₂ Ta(C ₃ H ₅)	assignment
A	5.5	5.5	5.6	5.5	metal d
B	7.8	7.8	(8.0)	(7.9)	allyl n. b. π
C	8.6	8.3	8.6	8.4	Cp
D	9.1	8.9	9.2	8.9	Cp
E	(9.4)	(9.5)	(9.6)	(9.7)	allyl

metal, involving M-C σ bonds. It is indeed tempting to compare the I. E. of band B to the I. E. of the M-C bonding orbital in the propyl complex. However for a localized description involving M-C σ bonds, the metal bonding orbital, combined with the π (C=C) orbital, should give rise to practically equivalent M-C bonds. It is however clear from the spectra that bands A and B differ dramatically in the amount of metal character and we therefore prefer the familiar σ donation- π acceptor scheme.

Cp₂Nb(C₃H₅), (MeCp)₂Nb(C₃H₅), Cp₂Ta(C₃H₅), (MeCp)₂Ta(C₃H₅)

Green *et al.* [4] have published the He(I) spectrum of Cp₂Nb(C₃H₅). Their assignment can be confirmed using He(I)/He(II) cross section variations, substituent effects and by varying the metal. Again the spectra are very similar and only the He(I) and He(II) spectra of CpNbC₃H₅ will be presented here (Fig. 6). Band A originates from the metal d-orbital

which can in principle interact with the π^* C₃H₅ orbital. However this π backbonding interaction cannot be as large as in the olefin and carbonyl complexes since upon comparing the very low I. E. of this band with the I. E. of the metal band in the latter complexes, a destabilization of nearly 1 eV is found.

Band B originates from the non-bonding π orbital of the allyl ligand (the a₂ orbital in the free ion) which interacts with the empty d_{yz} orbital. The broad C, D band contains again the Cp ionizations. The π bonding allyl orbital will be more stable and cannot be unambiguously assigned. It is possible that band E, which must be an allyl ionization, originates from this π orbital.

The dihalide complexes Cp₂ML₂

Cp₂ML₂ (L = halogen) complexes have been extensively studied by Green and coworkers [1]. They have found large differences in bandform in the Cp, Cl region (8.12 eV) upon variation of the metal. He(I)/He(II) intensity changes indicate severe overlapping of Cp and Cl bands for (MeCp)₂NbCl₂ and Cp₂TaCl₂. We have recorded Cp₂NbCl₂ and (MeCp)₂TaCl₂ and the results for these four compounds are presented in Table IV.

Using the systematic trends we found in the other classes of compounds it is possible to assign the spectra in somewhat more detail. Firstly M-Cl and *n*_{Cl} type orbitals are expected to be rather sensitive to metal variation while the Cp orbitals will be more sensitive to methylation of the Cp ring.

Secondly when interpreting cross sections in first order in terms of AO contributions [10] it can be predicted that the intensity decreases on going from He(I) to He(II) radiation becomes larger in the following order Cp < M-Cl < *n*_{Cl}.

Based on these arguments band D can be unambiguously assigned to ionization from Cp π orbitals. Bands E and F are rather insensitive to

Fig. 6. The He I and He II PE spectra of Cp₂Nb(C₃H₅).

Table IV. Ionization energies of the halide complexes.

	Cp ₂ NbCl ₂	(MeCp) ₂ NbCl ₂	Cp ₂ TaCl ₂	(MeCp) ₂ TaCl ₂	Assignment
A	6.8	6.5	6.4	6.2	a ₁ d ¹ (a ₁)
B	(8.7)	(8.5)	(8.8)	(8.6)	Cp, M-Cl
C	9.0	8.9	9.2	9.0	
D	10.2	9.8	10.1	9.8	Cp
E	(10.5)	(10.4)	(10.5)	(10.5)	<i>n</i> _{Cl} , M-Cl
F	10.9	10.9	11.1	11.1	

methylation and can thus be assigned to *n*_{Cl} and M-Cl orbitals. Bands B and C which are sensitive to methylation should then contain the remaining Cp ionizations and regarding the decrease in intensity on going from He(I) to He(II) some other *n*_{Cl} or M-Cl orbitals.

A more detailed assignment cannot be given owing to the overlapping of these bands.

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