Abstract: The electronic structures of trichloro[(1,2,3,3a,7a-η)-1H-inden-1-yl]-hafnium and bis(cyclopentadienyl)hafnium dichloride have been investigated by HeI and HeII UV photoelectron spectroscopy and DFT/OVGF calculations. The chlorine lone pair ionization energies are reduced considerably on going from HfCl4 to metallocene hafnium chlorides. The electronic structure results have been related to the mechanism of olefin polymerization catalysed by hafnocenes.

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Electronic structure of two catalytically important hafnocenes

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Abstract: The electronic structures of trichloro[(1,2,3,3a,7a-η)-1H-inden-1-yl]-hafnium and bis(cyclopentadienyl)hafnium dichloride have been investigated by HeI and HeII UV photoelectron spectroscopy and DFT/OVGF calculations. The chlorine lone pair ionization energies are reduced considerably on going from $HfCl_4$ to metallocene hafnium chlorides. The electronic structure results have been related to the mechanism of olefin polymerization catalysed by hafnocenes.

1. Introduction

Hafnocenes are complexes which have important practical applications as catalysts in the olefin polymerization processes [1a]. Several computational studies of mechanisms of this catalyzed polymerization have been reported recently [1b,1c]. The mechanistic studies have shown that cyclopentadienyl (Cp) and indenyl (Ind) ligands bound to hafnium influence ethane insertion and chain propagation in the catalyzed polymerisation cycle.

The relative stability of the cationic monomethyl form originating in the activation step of the catalyzed polymerisation was established to be an important factor in determining the efficacy of different catalysts [1b,1c]. The previous studies have also established that the nature of hafnium bonded ligand is the important factor determining catalytic efficacy because it affects the stability of the cationic form and energy of the first transition state in the catalytic mechanism. Aromatic ligands which are themselves electron donating towards hafnium and/or which contain electron donating substituents increase the stability of the cation, lower the transition state energy and hence enhance catalytic efficacy. The electron withdrawing substituents/ligands have the opposite effect. UV photoelectron spectroscopy can provide precisely such information about the relative electron donating properties of ligands coordinated to hafnium.

Therefore, since the electronic structure of ligands (in particular their electron donating properties) in hafnocene catalysts was shown to be very important, we have performed the electronic structure study of two hafnocenes containing different ligands by UV photoelectron spectroscopy.

2. Experimental and Computational methods

The samples of compounds shown below were purchased from Aldrich and used without further purification after checking their identity and purity by NMR spectroscopy.

I   **II**
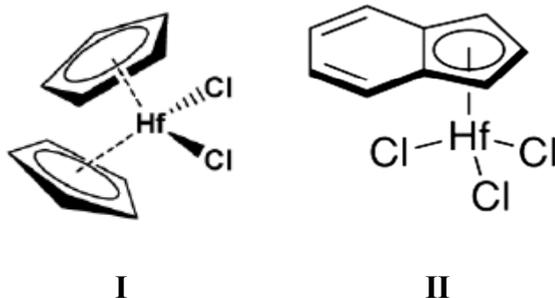
The HeI/HeII photoelectron spectra (UPS) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 meV and 70 meV, respectively when measured as FWHM of the $3p^{-1}$ $^2P_{3/2}$ Ar^+ $\leftarrow$ Ar ($^1S_0$) line.   The samples were studied with the inlet probe heated to 150 and 140 ^{o}C, respectively. The spectra obtained were reproducible and showed no signs of major decomposition with only a trace of HCl recorded (Fig. 2). Decomposition is usually demonstrated by the appearance of intense sharp peaks which are due to the presence of small molecules/decomposition products in the spectrometer's ionization chamber.

The quantum chemical calculations were performed with Gaussian 03 program [2] and included full geometry optimization of neutral molecules using B3LYP functional and Stuttgart effective core potentials for all atoms. The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT geometry was used as the input into the single point calculation using the outer-valence Green's function (OVGF) method

and the same basis set [3]. This method obviates the need for using Koopmans approximation and provides vertical and adiabatic ionization energies with typical deviation of 0.3-0.5 eV (depending on the size of the basis set) from the experimental values. The OVGF method was successfully used previously to analyze the photoelectron spectra of metallocenes [4]. The optimized geometry of Cp_2HfCl_2 corresponded within 0.01 Å and 1° to the experimental geometry determined by X-ray diffraction [5]. The geometry of $IndHfCl_3$ has not been reported.

3. Results and Discussion

The photoelectron spectra of the molecules studied are shown in Figs. 1-2. The assignments are summarized in Table 1 and are based on the results of OVGF calculations, HeI/HeII intensity variations and comparison with photoelectron spectra of related molecules: metallocenes containing Cp and Ind ligands [6,7], indene [8a] and cyclopentadienyl radical [8b]. Hafnium complexes studied in this work represent d^0 metallocenes.

Cyclopentadienyl derivative (**I**)

The HeI photoelectron spectrum shown in Fig. 1 is consistent with the previously reported HeI spectrum of Cp_2HfCl_2 [6]. The previously reported assignment was based on semiempirical CNDO calculations and did not provide detailed band assignments. **I** is a d^0 bent-metallocene and its spectrum is not expected to exhibit any bands at ionization energies <8 eV which usually correspond to metal d orbital ionizations. Indeed, none were observed which suggests that the bands in the 8.0-12.5 eV region correspond to ionizations from ligand based orbitals: cyclopentadienyl π-orbitals (π_{Cp}) and chlorine lone pairs (n_{Cl}). We have performed variable photon energy study not in order to repeat the previous work [6], but to distinguish experimentally between ionizations originating from chlorine and Cp ligands. The relative intensity

of chlorine lone pair ionization bands (n_{Cl}) is expected to decrease significantly on going from HeI to HeII radiation in view of the fact that atomic photoionization cross-section ratios at HeII/HeI energies are 0.05 and 0.31 for Cl3p and C2p orbitals, respectively [9]. The bands in the region 10.6-11.5 eV exhibit significant intensity decrease and can thus be unambiguously assigned to chlorine lone pair ionizations. The bands in the 8.6-9.2 eV region correspond to the ionization of predominantly Cp ligand π-orbitals. The analysis of AO composition of HOMO in **I** has shown that it contains 28% of Cl3p character in addition to predominantly C2p character originating from Cp ligands and small (6%) contribution from the metal. This amount of Cl3p character is similar to the amount of Cl3p character observed in the HOMO of HfCl$_4$ [10]. The relative intensity of the 8.6-9.2 eV band manifold also varies at HeI and HeII radiation. The 8.6-9.2 eV manifold shows small relative intensity decrease on going from HeI to HeII which is consistent with the small amount of Cl3p character present in the HOMO. The HeII/HeI atomic photoionization cross-section ratios for Hf6s and Hf5d orbitals are 1.05 and 0.24, respectively but due to very small metal contribution to high lying orbitals their influence on band intensity changes is very small [9].

Indenyl derivative (**II**)

The photoelectron spectra of **II** are shown in Fig. 2. The assignment of the spectra summarized in Table 1, was achieved by comparison with OVGF calculations, relative HeII/HeI band intensity changes and comparison with the spectra of indene [8a] and HfCl $_4$ [10]. The HeII/HeI intensities allow us (as in the analysis described previously for **I**) to clearly distinguish between chlorine lone pair ionizations which correspond to bands in the 10.95-12.1 eV region and Cp ligand π-orbital ionizations which correspond to three bands at 8.45, 9.35 and 10.30 eV. The HOMO whose

ionization appears at 8.45 eV does not contain any significant amount of Cl3p character (unlike **I**) but has predominantly C2p character with only 8% of metal character.

The ionization energies of chlorine lone pairs in **I** and **II** (Table 1) are significantly reduced compared to $HfCl_4$ where they appear in the 12.03-13.4 eV range. Comparison of the HOMO π-ionization energies in indene (8.16 eV) [8a] and **II** (8.45 eV) shows HOMO stabilization by approximately 0.3 eV upon $IndHfCl_3$ formation which is due to metal-ligand bonding. On the other hand, comparison of the HOMO π-ionization energies of Cp radical (8.43 eV) [8b] and **I** (8.6 eV), reveals smaller stabilization amounting to 0.17 eV. HOMO ionization energy in **I** is 0.15 eV higher than in **II** due to the admixture of Cl3p orbitals in the former. We conclude that the ligand-hafnium bonding and electron transfer interactions in **II** are stronger than in **I**. The bound Cp ligand has higher HOMO ionization energy than the bound Ind ligand.

Electronic structure related to catalysis

The previous studies of metallocenes containing indenyl ligands bound to iron, cobalt or ruthenium have suggested that electron-rich Ind is more electron releasing ligand then Cp [7]. The catalytic mechanism involving hafnocenes is complex and involves many intermediates and transition states which pertain to the catalyst-ethene complex [1]. Activation of the catalyst leads to the generation of cationic monomethyl form which can then coordinate the ethene monomer. Stability of the monomethyl form influences the activation barrier and the feasibility of the activation step in the catalytic mechanism. The structures and energies of various catalyst-ethene π-complexes have been calculated [1b,c]. Our results indicate that Ind ligand is more electron-donating than Cp as can be seen from the comparison of the HOMO ionization energies in **I** and **II**. The HOMO energy in **II** is approximately 8.6-

8.45=0.15 eV= 15 kJ/mol lower than in **I**. The ligand properties will affect the stabilities of reactant molecules themselves, the stability of cationic monomethyl forms and corresponding activation energy barriers. Since the activation energies strongly influence the kinetics of catalytic process we compare the differences in activation energies when different ligands are present in the hafnocene catalysts. The calculated differences in activation energies (for different ligands) in chain propagation and chain termination steps in ethene polymerization catalyzed by hafnocenes were 23.1 and 17.4 kJ/mol, respectively [1b,1c]. These differences in activation energies compare favorably with our value of 15 kJ/mol which refers to a single Ind bound ligand. Assuming that when two identical ligands (Cp or Ind) are present the influence on activation energy difference shall be doubly effective, we arrive at the approximate value of 30 kJ/mol which quantifies the stabilizing effect of individual Ind ligand compared to the individual Cp ligand on activation energy differences. This value is comparable to the calculated values of 23.1 and 17.4 kJ/mol discussed above. The agreement is not perfect because the calculated values involve approximations in the quantum mechanical methods used and also because the electronic structure properties are not the only factors effecting activation energies.

4. Conclusion

Our study leads to two important conclusions. In hafnocenes, the Ind ligand is more electron-releasing than the Cp ligand. The electron releasing potency of the Ind ligand compares well with the calculated activation energy differences in reaction steps of catalyzed olefin polymerization. The comparison is of qualitative nature since several approximations have been made in the calculations of catalytic cycles e.g. the absence of co-catalyst. It is gratifying however that the electronic structure result is in good agreement with the calculations on catalytic mechanisms. UPS data can thus be used

to help assess relative efficacy of different hafnocene catalysts and direct synthetic efforts towards the preparation of new, more efficient catalysts.

Acknowledgement

Table 1. Experimental (E_i/eV) and calculated (OVGF/eV) vertical ionization

energies, orbital assignments and relative band intensities in metallocenes[a]

Compound	Band	E_i	OVGF	Assignment	Relative Band Area HeII/HeI
I	*X*	8.6	8.46	π_{Cp}	1.0
	A-B	9.2	8.93, 9.07	π_{Cp} , π_{Cp}	
	C	10.05	9.76	π_{Cp}	1.1
	D	10.6	10.47	σ_{Cp}	0.21
	E-I	11.25 (11.5)	11.04, 11.10, 11.14, 11.42, 11.58	n_{Cl}, n_{Cl}, n_{Cl}, n_{Cl}	0.21
II	*X*	8.45	8.30	π_{In}	1.0
	A	9.35	9.17	π_{In}	0.76
	B	10.30	10.37	π_{In}	0.45
	C	10.95	10.90	n_{Cl}	0.20
	D-H	11.5-12.1	11.17, 11.59, 11.88 11.97, 12.08	n_{Cl}	0.20

[a]the numbers in brackets correspond to shoulders (overlapping bands)

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Figure captions

Fig. 1 HeI and HeII photoelectron spectra of **I**
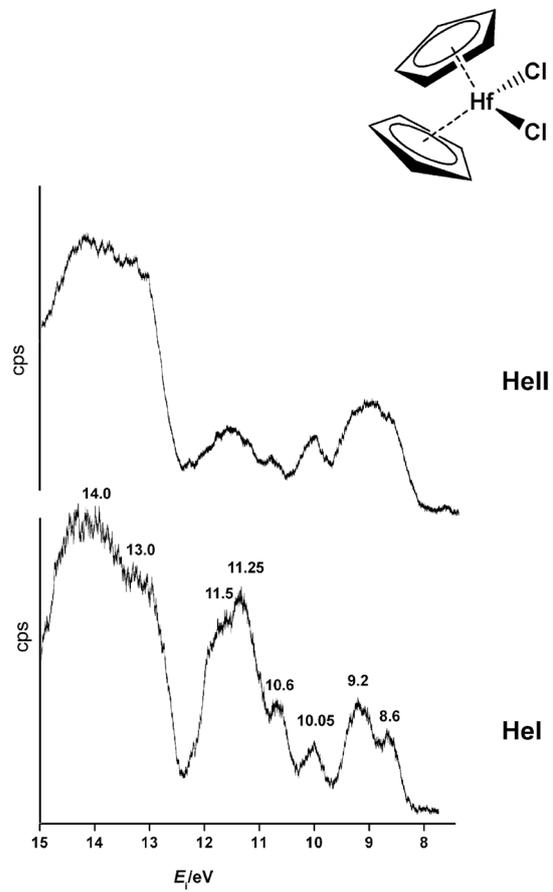
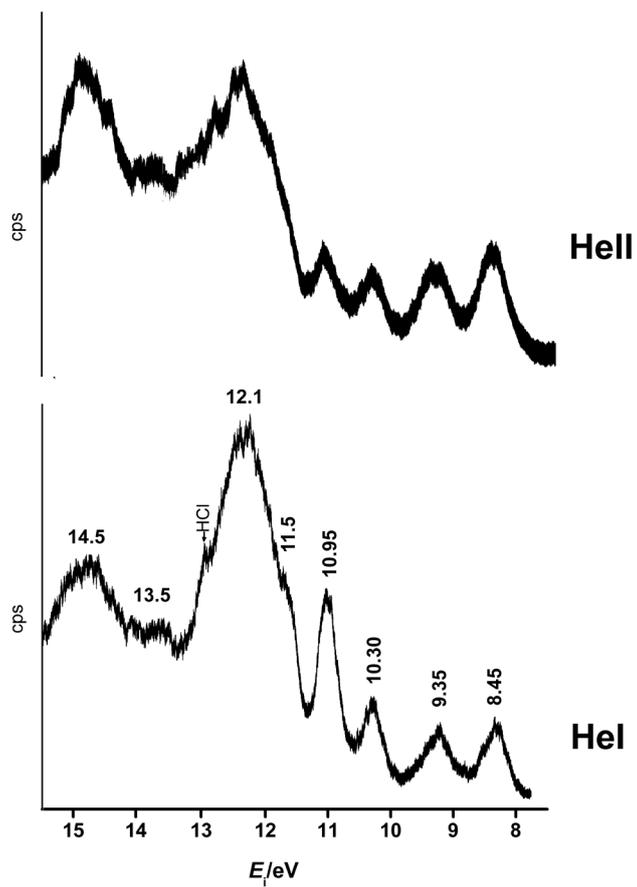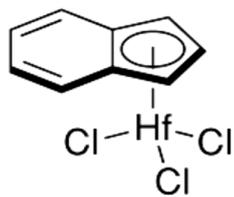Fig. 2 HeI and HeII photoelectron spectra of **II**

Fig. 1

Fig.2