Application of Ultraviolet Photoelectron Spectroscopy to Molecular Properties. Part 27.† Stereochemistry of Ligand Exchange Reactions of Titanocene Derivatives‡

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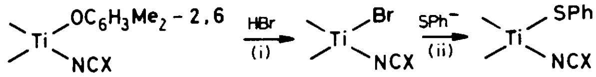
The electronic structure of pseudohalogen (NCX, X = O or S) complexes of titanocene has been analyzed on the basis of He I and He II photoelectron data and extended Hückel results. This



analysis explains the stereoselectivity of the two exchange reactions (i) and (ii) which depends on the heteroatom X [for reaction (i), X = O and S, retention; for reaction (ii), X = S, retention; X = O, inversion].

The chemistry of bent metallocenes of the type $[M(cp)_2L_n]$ (cp = η-cyclopentadienyl) has undergone considerable progress during the past few years, especially in the field of their synthesis and reactivity.[1] The analysis of the electronic structure of these compounds has been the object of several theoretical[2-4] and spectroscopic studies; u.v. photoelectron spectroscopy (u.p.e.s.) has been used primarily in these studies.[4-9] In the special case where the metal atom belongs to Group 4 (Ti, Zr, or Hf), theoretical and spectroscopic studies have dealt primarily with metallocenes having halogen ligands (L)[10-12] and more recently with sulphur and selenium ligands.[10]

The present work deals with titanocenes with isocyanate (NCO), isothiocyanate (NCS), and phenolate (OPh) ligands. Experimentally, the stereochemistry of the nucleophilic substitution products varies with the nature of L. We thus analyzed the effect of ligands on the electronic structure of these complexes in order to use these data to understand more fully the different orientations occurring during nucleophilic attacks.

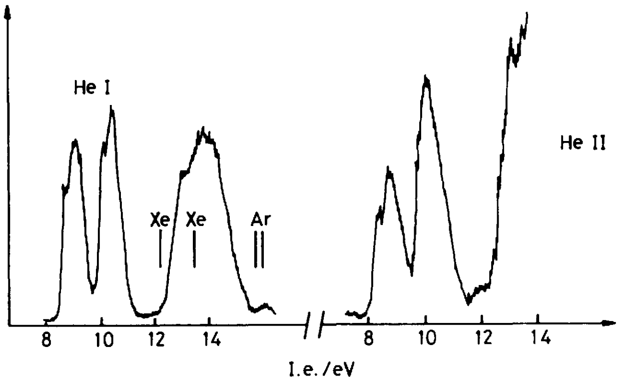


Figure 1. Photoelectron spectra of compound (1)

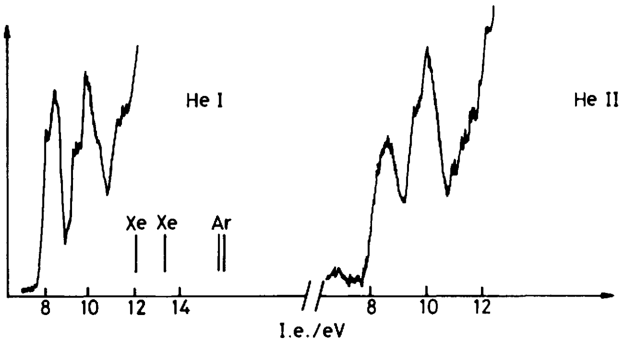


Figure 2. Photoelectron spectra of compound (3)

Results and Discussion

The photoelectron spectra (He I, He II) representative of the series of compounds are shown in Figures 1—6. Ionization potentials are shown in the Table.

Two different ionizing radiations were used, He I (21.21 eV) and He II (40.81 eV). This technique is a particularly effective assistance in assigning spectra. The intensity of photoelectron bands depends both on the type of orbital associated with the photoelectron removed and its kinetic energy, *i.e.* the energy of the ionizing radiation for a given ionization potential. Thus, using several well known qualitative rules, the comparison of band intensities recorded with the two radiations can help to determine the molecular orbitals associated with the ionization potentials. For example, if we take as a basis of comparison a molecular orbital (m.o.) localized in the 2*p* atomic orbitals (a.o.) of carbon, the m.o. localized on the 2*p* a.o. of nitrogen and oxygen will correspond to bands whose intensity increases in He II. Those localized on the 3*p* a.o. of sulphur or the 4*p* a.o. of bromine, however, will exhibit decreasing band intensity when the radiation is changed from He I to He II.

The molecular orbitals of the $Ti(cp)_2$ fragment have been described in previous publications.[12,13] The first four occupied π-type orbitals are localized primarily on the rings. In the order of increasing stability, they present b_1, a_2, b_2, and a_1 symmetries (in the case of C_{2v} molecular symmetry). The *d* orbitals of titanium are vacant as a result of the formal transfer of two electrons from the metal to the cyclopentadienyl rings.

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† Part 26, C. Lafon, D. Gonbeau, G. Pfister-Guillouzo, M. C. Lasne, J. L. Ripoll, and J. M. Denis, *Nouv. J. Chim.*, 1986, **10**, 69.

‡ *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

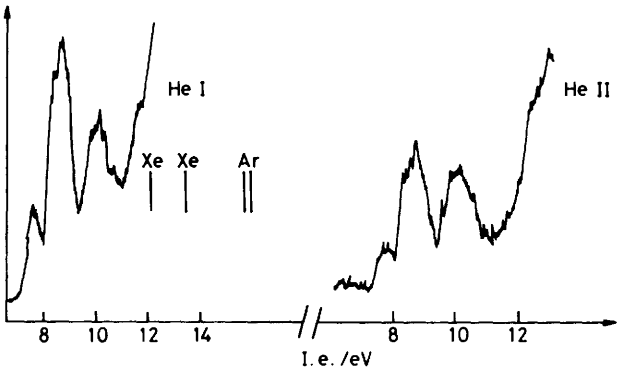


Figure 3. Photoelectron spectra of compound (**5**)

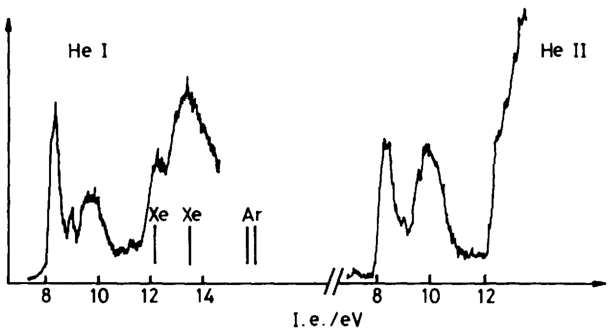


Figure 4. Photoelectron spectra of compound (**6**)

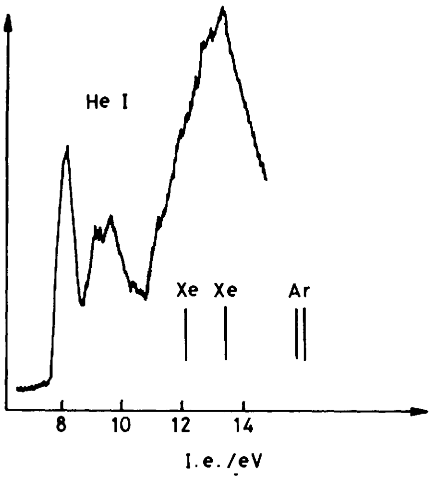


Figure 5. Photoelectron spectra of compound (**8**)

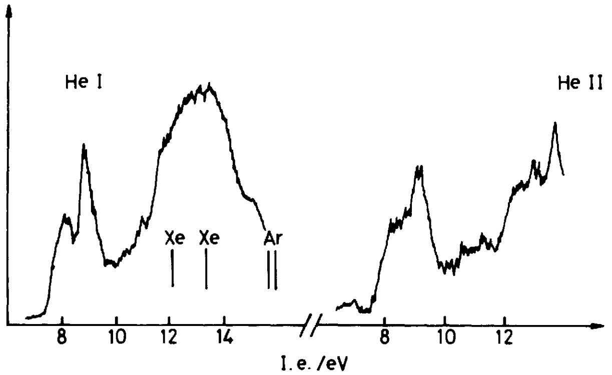


Figure 6. Photoelectron spectra of compound (**9**)

The NCX fragments (X = O or S) present two orthogonal π systems. In the absence of any interaction, the two least stable occupied orbitals are degenerate and of the π type (one in the π plane, the other in the σ plane, orbitals located in the TiL′ plane). In addition, they are localized on the two heteroatoms N and X and present a node close to the central C atom. In the case of complexes with symmetrical ligands (L = L′ = NCX) and thus with C_{2v} symmetry, these two orbitals form combinations with b_2, a_2, b_1, and a_1 symmetries, in the order of increasing stability. This order depends on the degree of interaction between the localized orbitals, *i.e.* their degree of overlap. Thus, the large overlap of the orbitals located in the TiL′ plane induces a greater gap of b_2 and a_1 combinations in comparison to that of the π orbitals (a_2 and b_1 combinations).

These combinations interact with orbitals having the same symmetry on the other fragments of the molecule, especially with the π orbitals of the cyclopentadienyl fragments. The overlap between these orbitals is relatively weak, and so these interactions occur *via* the *d* orbitals of the metal. In the case of C_{2v} molecular symmetry, these orbitals have the following respective symmetries: a_1 for d_{z^2} and $d_{x^2-y^2}$, a_2 for d_{xy}, b_1 for d_{xz} and b_2 for d_{yz}. The sequence of molecular orbitals arising from this type of 'through-bond' interaction depends on the relative energy position of the orbital localized on the fragments. Thus, the last two occupied orbitals of HNCO are deeper than for its sulphur homologue: 11.62 and 12.13 eV for HNCO, 9.94 and 10.3 eV for HNCS.[14] The occupied orbitals of the phenol group are even less stable, at 8.7 and 9.39 eV,[15] and are localized primarily on the aromatic ring.

The first photoelectron bands of complexes with C_{2v} symmetry (L = L′ = NCX) can be unequivocally assigned from the changes in the respective intensities of He I and He II recording. In the case of the di-isocyanate compound (**1**), the intensity of the second broad band between 10 and 10.4 eV increases in He II in comparison to the rest of the spectrum. It can thus be assigned to the four orbitals localized on the NCO groups. The four orbitals of the cyclopentadienyl groups are thus less stable and correspond to the first band (ionization potential between 8.7 and 9.1 eV). When two hydrogens of one of the rings are replaced by a methyl and an isopropyl group [compound (**2**)], a general destabilization of all the orbitals is observed. This shows the effective interaction of the orbitals localized on the different fragments of the molecule (cp rings and NCO groups). This attribution is confirmed by the slightly greater shift of the first band (between 0.35 and 0.4 eV) in comparison to that of the second (between 0.25 and 0.3 eV, Table).

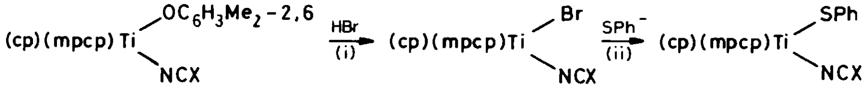
The intensity of the first two bands of the homologous sulphur compounds (**6**) and (**7**) decreases strongly in He II. They are thus associated with orbitals localized primarily on the sulphur atom of the NCS groups. In the light of the respective intensities of these two bands, it would appear that the first can be attributed to three ionic states ($^2B_2$, $^2A_2$, and $^2B_1$) and the second to a single state ($^2A_1$). The greater gap of b_2 and a_1 combinations observed for the sulphur compounds (*ca.* 0.7 eV) in comparison to that observed for the oxygen compounds (*ca.* 0.5 eV) suggests in the first case a greater stabilization of the a_1 orbital by the vacant d_{z^2} orbital of titanium, as a result of their greater energy proximity (the NCS orbitals are *ca.* 1.5 eV higher than those of NCO). As in the case of (**1**) and (**2**), substitution of the cyclopentadienyl rings shifts all photoelectron bands towards lower energies. The first potentials associated with orbitals localized primarily on the NCS groups decrease by 0.25 to 0.3 eV, while those associated with the rings decrease by 0.35 to 0.45 eV (Table).

The resulting through-bond interaction between the orbitals of the cyclopentadienyl and NCX groups is shown not only by

Table. Ionization potentials of the complexes [Ti(cp)$_2$LL′] and some derivatives[a]

Cyclopentadienyls[b]	L	L′	Experimental ionization potentials (eV)					
(**1**) cp cp	NCO	NCO	8.7	9.1	10 ↗	10.4 ↗		
(**2**) cp mpcp	NCO	NCO	8.3	8.75	9.7 ↗	10.15 ↗		
(**3**) cp mpcp	NCO	Br	8.1	8.55	9.4 ↗	9.9 ↗	10.4 ↗	11.8
(**4**) cp cp	NCO	$OC_6H_4CH_3$	7.75	8.35	8.8	9.95 ↗	10.2 ↗	
(**5**) cp cp	NCO	$OC_6H_3(CH_3)_2$	7.55 ↘	8.35 ↘	8.65	9.85 ↗	10.15 ↗	
(**6**) cp cp	NCS	NCS	8.4	9.05	9.6	9.85	12.2	
(**7**) pcp pcp	NCS	NCS	8.1 ↘	8.8 ↘	9.15	9.5		
(**8**) cp mpcp	NCS	Br	8.2	9.15	9.65	10.4	11.25	
(**9**) cp cp	NCS	$OC_6H_4CH_3$	7.75	8.20	8.90	9.2		

[a] ↗ Bands increasing in intensity with He II radiation; ↘ bands decreasing in intensity with He II radiation. [b] Abbreviations: cp = cyclopentadienyl, pcp = isopropylcyclopentadienyl, mpcp = 1-methyl-2-isopropylcyclopentadienyl.



the substitution effects discussed above, but primarily by the ionization potential values of the π orbitals of the rings. Whereas in compound (**1**) the values of these potentials are comparable to those of dialkyl metallocenes,[10] the presence of NCS groups with less stable occupied orbitals shifts the potentials of the cyclopentadienyl groups of compound (**6**) by almost 1 eV.

When the NCO group is replaced by a bromine atom [compound (3)], the intensity of the first band of the spectrum decreases (Figure 2), showing the effective participation of the atomic orbitals of bromine in the highest occupied molecular orbitals (h.o.m.o.s). These assignments are supported by comparison with the p.e. spectra of homologous dihalogen complexes.[12] Indeed the energies of chlorine and iodine p_π orbitals are respectively close to the h.o.m.o.s of the NCO and NCS fragments. Thus we find the same sequence of m.o.s between [Ti(cp)$_2$(NCO)$_2$] and [Ti(cp)$_2$Cl$_2$], or [Ti(cp)$_2$(NCS)$_2$] and [Ti(cp)$_2$I$_2$].

The substitution of an NCO group by a phenolate group [compounds (**4**) and (**5**)] results in the appearance of an additional low-energy band (between 7.55 and 7.75 eV). This band, a bit more sensitive to a substitution on the phenyl ring [passage from (**4**) to (**5**)] is associated with the orbital with local b_1 symmetry, localized on the aromatic ring. The corresponding orbital with local a_2 symmetry (these two orbitals are degenerate in benzene) corresponds to the second band of the spectrum (which also includes the bands associated with cp), *i.e.* ionization potential of 8.8 eV for (**4**) and 8.65 eV for (**5**) (Table, Figure 3).

In the case of the homologous sulphur compound (**9**), the energies of the b_1 orbital of the benzene group and the h.o.m.o. of the isothiocyanate group are very close and are associated with the first band between 7.75 and 8.2 eV (Figure 6). The second band, between 8.9 and 9.2 eV, results from the ionization of two other m.o.s localized on the NCS and phenoxy groups. The orbitals of the cyclopentadienyl groups correspond to the band with lowest intensity, located between 10 and 11 eV.

Stereochemistry of Titanocenes.—We have obtained[16] pairs of pseudohalogenated thioaryl diastereoisomers, derived from titanocene, by continuing the chain of nucleophilic substitutions (i) and (ii), starting with the corresponding pseudohalogenated aryl complexes (mpcp = 1-methyl-2-isopropylcyclopentadienyl, X = O or S).

If we start with a diastereoisomer of identical configuration, for X = O or S, the first step (i) (substitution of $OC_6H_3Me_2$-2,6 by Br^-) is totally selective and stereospecific. Stereospecificity corresponds to a retention of configuration (attack by Br^- on the side of the Ti–O bond). In the second step (ii), the substitution remains selective (the only co-ordinate shifted is bromine) and partially stereospecific, but it corresponds to a majority inversion at the level of the titanium atom in the case of the isocyanate compound (attack on the Ti–NCO side), while in the case of the isothiocyanate compound, there is retention of configuration (attack on the Ti-Br side).

We attempted to interpret this stereochemistry from the electronic structure of the compounds participating in the two reaction steps (i) and (ii). If these nucleophilic substitutions are governed by the frontier orbitals, their stereochemistry must depend predominantly on the overlap between the vacant orbitals with lowest energies of the complex and the h.o.m.o.s of the nucleophile, in the transition state. This state will be more stable as there is a greater degree of overlap between these orbitals. This overlap depends not only on the localization of the orbitals on the different atoms, but also on their sign (lobes in phase or out of phase).

Substrates (**4**) and (**9**) were chosen as model starting molecules for this study. The lowest unoccupied molecular orbital (l.u.m.o.) in these compounds has primarily the $d_{x^2-y^2}$ and d_{z^2} character of titanium. It presents a node on each Ti–O and Ti–N bond; the lobes on oxygen and nitrogen are out of phase with the $d_{x^2-y^2}$ and d_{z^2} orbitals (Figure 7). This weakens the overlap of this l.u.m.o. with the occupied orbital of the nucleophile (h.o.m.o.), more so since the vacant orbital has a pronounced localization on the heteroatom. This localization depends to a large extent on the interaction between the vacant 3*d* orbitals of titanium and the h.o.m.o.s localized on the OPh and NCO (or NCS) fragments. Localization will be greater if the latter orbitals are less stable, *i.e.* energetically closer to the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of the metal. For both compounds (**4**) and (**9**), the localization of the l.u.m.o. is slightly greater on the NCX part than on the phenol oxygen. This results in good agreement, with the higher stability of the orbital localized on this oxygen (11.6 eV in phenol) in comparison to those of the NCO and NCS groups.* Attack by the halogen on the two types

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* These qualitative arguments on the interactions between the vacant Ti 3*d* orbitals and the h.o.m.o.s of the different ligands are consistent with the localization of the l.u.m.o. of [Ti(cp)$_2$I$_2$] calculated by the extended Hückel method[2,17] (on the geometric structures taken from the literature[18,19]).

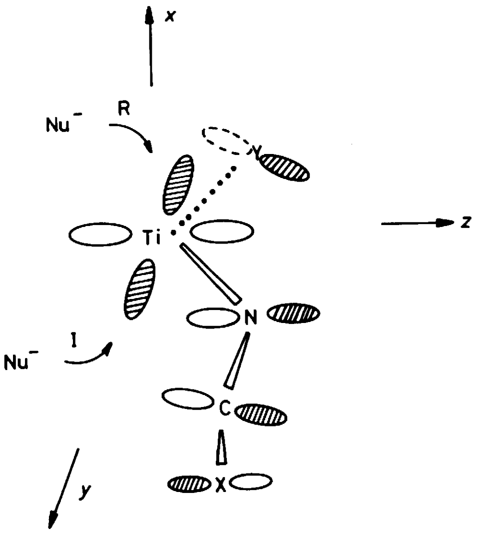

Figure 7. Localization of the l.u.m.o. in the yOz plane (the lobes of $d_{x^2-y^2}$ and d_{z^2} orbitals out of this plane have been omitted); X = O or S, Y = O or Br; Nu⁻ = nucleophile; I = inversion; R = retention

of compounds (**4**) and (**9**), which must occur preferentially on the side of the ligand participating the least in the most stable vacant orbital of the complex, will thus occur on the side of the phenol oxygen. This is a reaction with retention of configuration at the level of the titanium atom during the stereochemical progression of the reaction (i).

In the case of brominated complexes, the l.u.m.o. differs as a function of the NCX group [X = O for (**3**), S for (**8**)]. Although this orbital still has primarily the $d_{x^2-y^2}$ and d_{z^2} character of titanium, it is localized to a much greater extent on bromine in compound (**3**) (the participation of nitrogen is practically nil because of the relative stability of the occupied m.o. of NCO in comparison to those of Br) and, on the contrary, on the NCS group in compound (**8**), whose m.o.s are less stable than bromine. It follows that nucleophilic attack will take place on the side of the Ti–N bond of (**3**) (inversion of configuration) and on the side of the Ti–Br bond in (**8**) (retention of configuration).

Conclusions

The analysis of u.p.e. spectra (He I and He II) has led to the demonstration of a strong through-bond interaction between the orbitals of the ligands (NCX, Br, OPh) and the two cyclopentadienyl groups. This results in an inversion in the sequence of the h.o.m.o.s between the isocyanate and isothiocyanate complexes.

The energy position of the occupied orbitals, semi-localized on the ligands, is also directly related to the localization of vacant orbitals. Thus, we were able to explain the stereospecificity of the two exchange reactions $\geqslant$TiOPh $\longrightarrow$ $\geqslant$TiBr and $\geqslant$TiBr $\longrightarrow$ $\geqslant$TiSPh. These reactions are controlled by the frontier orbitals and depend primarily on the degree of stabilizing interactions in the transition states between the h.o.m.o.s of the attacking nucleophile and the l.u.m.o.s of the complex.

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