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He(I) and He(II) Photoelectron Spectra of Hpyrrole-2-CH=N′–t-Bu and the Biscarbonyl Rh(I) and Ir(I) Complexes of its Anion

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Abstract

The He(I) and He(II) photoelectron spectra of a series of [(L–L)M(CO)$_2$] (L–L = pyrrole-2-CH=N′–R; R = t-Bu; M = Rh, Ir) complexes are reported. Assignments are proposed based on He(I)/He(II) intensity differences, on molecular orbital calculations of related complexes and of free ligands, and by comparison with the spectra of the free ligands Hpyrrole-2-CH=N′–t-Bu, Hpyrrole-2-carbaldehyde and Hpyrrole.

The electronic structure of the complexes is discussed and conclusions are drawn about the metal–ligand interaction.

Introduction

During the last decade in our laboratory there has been much interest in the properties of α-diimine ligands and their transition metal complexes [1–6]. Attention has been paid to the chemistry of such systems [6, 7], as well as to their metal-to-ligand charge transfer photochemistry [1–5]. The backbone of these ligands is the –N=CH–CH=N– skeleton, which is capable of σ-donation via the nitrogen lone pairs towards the metal, while π-backbonding can take place from the metal into the lowest π* orbital of the ligand [5–8]. Since UV photoelectron spectroscopy (UPS) is probably the most direct method to determine the electronic structure of molecules, we have used this technique to study in detail several series of (α-diimine) transition metal carbonyl complexes [9–11].

In this paper we report the He(I) and He(II) photoelectron (PE) spectra of a series of [(L–L)-M(CO)$_2$] complexes, where L–L is the anion of a pyrrole-2-imine (pyrrole-2-CH=N′–t-Bu)** and M is rhodium or iridium (Fig. 1, 5). These ligands have been the subject of many studies concerning the bonding of polydentate nitrogen donor ligand towards Cu(I), Ag(I) and Zn(II). Most of this work has been performed by van Stein *et al.* [12]; while van Dam *et al.* [13] reported the first UPS data of square planar Rh(I) and Ir(I) complexes with a related monoanionic β-diketonate ligand.

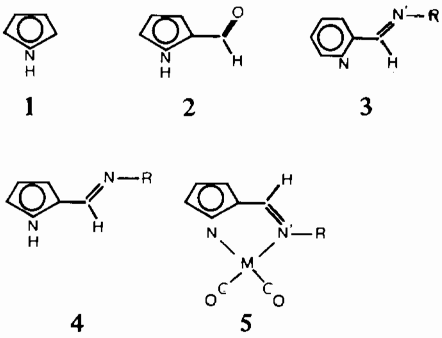

Fig. 1. The structure of the free ligands: (1) Hpyrrole, (2) Hpyrrole-2-CHO, (3) pyridine-2-CH=N′–R, R = i-Pr, (4) Hpyrrole-2-CH=N′–R, R = t-Bu and (5) bonding mode in square planar complexes [(pyrrole-2-CH=N′–t-Bu)M(CO)$_2$] (M = Rh, Ir).

Experimental

Syntheses

The free ligand Hpyrrole-2-CH=N′–t-Bu was prepared by condensation of Hpyrrole-2-carbaldehyde and NH$_2$–t-Bu in diethylether according to the literature [12]. The complexes were prepared according to the method described by Bonati and Wilkinson [14]. The compounds were checked for purity by elementary analyses, ^{1}H NMR and IR. The thermal stability of the complexes in the gas phase was checked by heating them in vacuum in a Mettler Thermo-analyser type 1. No decomposition was found.

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**Throughout this paper, for economy of space, we will make use of the following abbreviations: Hpyrrole = H_5C_4N aromatic; pyrrole$^-$ = H_4C_4N monoanion; Hpyrrole-2-CH=N′–R = substituted Hpyrrole on the C$_2$ atom (Fig. 1, 1) (R = t-Bu = tert. butyl; R = i-Pr isopropyl).

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Photoelectron Spectra

The spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer modified with a Helectros He(I)/He(II) source. The spectra were calibrated using Ar and Xe lines as internal calibrants.

Results and Discussion

In dealing with ionizations, the validity of Koopman's theory [15] will implicitly be assumed, so each ionization will be identified with a molecular orbital. Chemically speaking, molecular orbitals are either highly localized or they consist of simple combinations of localized orbitals. In UPS this model view has the advantage that use can be made of empirical assignment criteria such as He(I) and He(II) intensity differences and shift effects upon substitution. Ionization cross sections of atomic orbitals are well tabulated for elements up to Cl [16].

Transition metal d-orbitals are commonly found to possess a moderate He(I) and a high He(II) cross-section. This has been of great use in assigning the UP spectra of many transition metal complexes [17]. Before presenting and discussing the UP spectra of the compounds it is worthwhile to breakdown the square planar molecules $[(L-L)M(CO)_2]$ into three parts.

First we have to consider the M 1+ ion. The eight valence electrons of Rh or Ir occupy four d-orbitals, the $d_{x^2-y^2}$ being empty and suited for σ-donation from the four coordinating ligand atoms.

The second part consists of the two carbonyl ligands. A CO ligand possesses as relevant valence orbitals two σ, 5σ (C character), 4σ (O character) and one π (1π). The ionization energies (IE) of these orbitals are always above 12 eV [9–11, 13, 17].

The last part is the ligand (L–L), which is the most complex and which consists of a Hpyrrole ring and an imine unit. The IEs of the two π orbitals (a_2 and b_1 in C_{2v}) of Hpyrrole are known from several studies [19, 20]. The IEs of $\pi_{CN'}$ and of the nitrogen lone pair orbital of N′ in the –CH=N′–R part are known from UP spectral data of R–N=CH–CH=NR [9–11, 20, 21] (R = t-Bu, i-Pr) and pyridine-2-imine (Fig. 1, **3**). Some level mixing of the π-orbitals of the two units can be expected.

Spectra of the Ligands (Fig. 1, 2 and 4)

The He(I) and He(II) photoelectron spectra of Hpyrrole-2-carbaldehyde (**2**) and Hpyrrole-2-CH=N′–t-Bu (**4**) are illustrated in Figs. 2 and 3 respectively and the observed vertical ionization energies are collected in Table I.

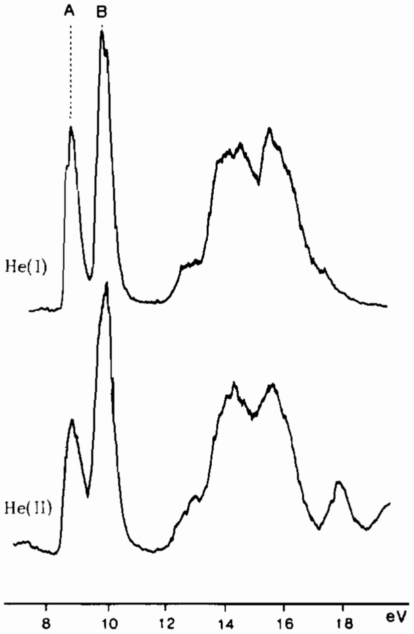

Fig. 2. He(I) and He(II) photoelectron spectra of Hpyrrole-2-CHO.

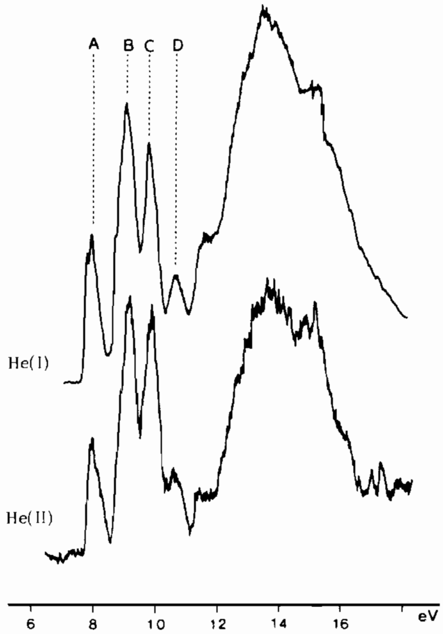

Fig. 3. He(I) and He(II) photoelectron spectra of Hpyrrole-2-CH=N′–t-Bu.

The assignment of the UP spectra of Hpyrrole-2-CHO is straightforward by comparison with Hpyrrole and formaldehyde. Band **A** at 8.77 eV belongs to ionizations from the π (a_2) orbitals of the pyrrole ring. This IE value is 0.54 eV higher than observed for Hpyrrole itself [18]. It will therefore be obvious that the second π (b_1) orbital will be found at an ionization energy which is about 0.99 eV higher than band **A** (= band **B** at 9.75 eV; Table I).

The intensity ratio of band **A**:**B** in the He(I) spectrum (Fig. 2) is however not 1:1, but more or less

1:2. This can be explained by a coincidence of the ionizations from this π (b_1) orbital with those from the oxygen lone pair (n_o) orbital. This decrease of the IE of n_o by 1 eV (9.8 eV compared with the value of 10.88 eV measured for HCHO [22]) is the opposite of the increase of IEs of the Hpyrrole ring due to inductive charge shifts towards the oxygen atom.

The presence of n_o participation in band **B** is evident from the He(II) spectrum. The intensity ratio of **A**:**B** is then increased to 1:3, in agreement with the cross sections for oxygen localized orbitals [16]. The IE value of n_o is in the same range as reported earlier by van Dam *et al.* [23] for crotonaldehyde.

The ionizations from the π_{CO} orbital can be expected above 12 eV and are obscured by ionizations from inner σ orbitals of the ligand.

The assignment of the UP spectra of Hpyrrole-2-CH=N'–t-Bu (Fig. 3) can now be made by comparison with the results discussed above. Bands **A** and **B** at 7.90 and 9.00 eV are assigned to $\pi(a_2)$ and $\pi(b_1)$ of the Hpyrrole unit respectively. These IE values are lowered by 0.33 and 0.22 eV respectively compared with Hpyrrole. This lowering is the same as has been found on going from pyridine to pyridine-2-CH=N'–i-Pr (Fig. 1, 3) [21].

The $n_{N'}$ lone pair ionization can be expected to be in the same range as for i-Pr-N=CH–CH=N–iPr (*trans*) [20, 9] and pyridine-2-CH=N'–i-Pr [21], which was about 9.7 eV. The band that arises from ionizations from this $n_{N'}$ orbital is observed at 9.71 eV and indicated with **C**. The remaining band below the onset at 11.5 eV is **D** at 10.53 eV. This band belongs to ionizations from the $\pi_{CN'}$ orbital, which was found at 10.7 eV for i-Pr–N=CH–CH=N–i-Pr ($\{\pi_1(+) + \pi_2(-)\} \div 2$) and at 11.2 eV for pyridine-2-CH=N'–i-Pr [21].

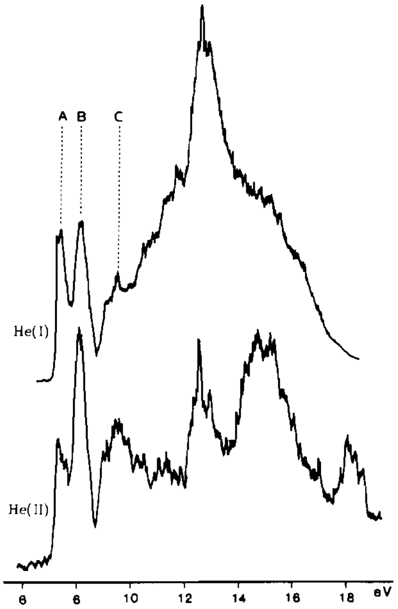

Fig. 4. He(I) and He(II) photoelectron spectra of [(pyrrole-2-CH=N'–t-Bu)Rh(CO)$_2$].

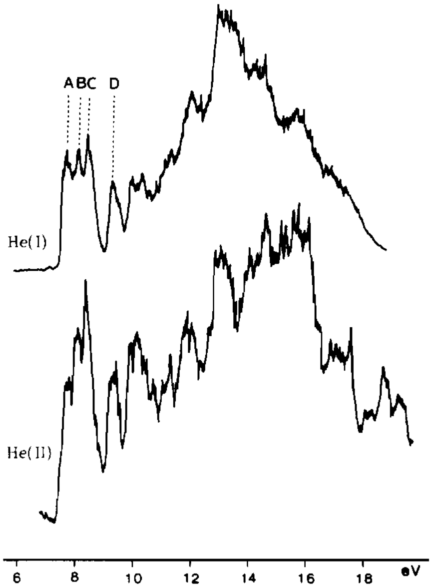

Fig. 5. He(I) and He(II) photoelectron spectra of [(pyrrole-2-CH=N'–t-Bu)Ir(CO)$_2$].

The broad band at higher energy is less structured and will not be discussed here, since no further information can be derived from this region. Now that we have assigned and discussed the ionizations of the ligand Hpyrrole-2-CH=N'–t-Bu, it is possible to investigate their Rh and Ir square planar bis carbonyl complexes.

Complexes [(Pyrrole-2-CH=N'–t-Bu)M(CO)$_2$] (M = Rh, Ir) (5)

The He(I) and He(II) photoelectron spectra of these two complexes are illustrated in Figs. 4 and 5 respectively. The observed vertical ionization energies are summarized in Table I.

TABLE I. Observed Vertical Ionization Energies (eV) for the Ligands Hpyrrole [18], Hpyrrole-2-CHO, Hpyrrole-2-CH=N'–t-Bu and the two Complexes [(Pyrrole-2-CH=N'–t-Bu)-M(CO)$_2$] (M = Rh, Ir), (Band indices in Brackets)

Compound	IE ± 0.05			
Hpyrrole [18]	8.23	9.22		
	π_2	π_1		
Hpyrrole-2-CHO	8.77 (**A**)	9.75 (**B**)		
	π_2	$\pi_1 + O_{lp}$		
Hpyrrole 2-CH=N-t-Bu	7.90 (**A**)	9.00 (**B**)	9.71 (**C**)	10.53 (**D**)
	π_2	π_1	$n_{N'}$	$\pi_{CN'}$
M = Rh	7.39 (**A**)	8.21 (**B**)	9.6 (**C**)	
	π_2	d + π	d	
M = Ir	7.71 (**A**)	8.10 (**B**)	8.40 (**C**)	9.52 (**D**)

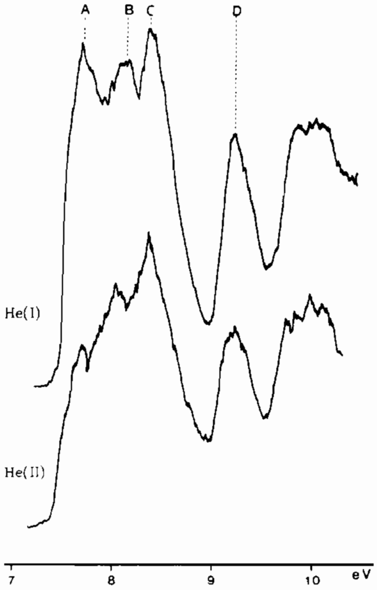

Fig. 6. Expanded low IE region He(I) and He(II) pe spectra of [(pyrrole-2-CH=N′–t-Bu)Ir(CO)$_2$].

For the [(pyrrole-2-CH=N′–t-Bu)Rh(CO)$_2$] complex only two (**A** and **B**) are observed in the low energy region (7–9 eV). The energy difference between **A** and **B** is 0.82 eV, which is slightly less than found between the corresponding bands of Hpyrrole (0.99 eV [18]) and Hpyrrole-2-CH=N′–t-Bu (1.10 eV). Band **A** still shows some vibrational structure ($\approx$1400 cm^{-1}) and this band is assigned to the π (a_2) orbital of the pyrrole ring of the ligand. Band **B** belongs to ionizations from the other π orbital of the pyrrole ring (b_1).

On going from He(I) to He(II) excitation the intensity ratio of band **A**:**B** changes dramatically, as can be seen from Fig. 4. This phenomenon is ascribed to participation of metal 4d-orbitals of rhodium in band **B**. The four occupied d-orbitals of Rh(I) d^8 transform is C_s-symmetry as a′(d_{z^2}), a″(d_{xz}), a′(d_{xy}) and a″(d_{yz}). Two of these (a″) are suitable for π-backdonation into the π^* orbitals of the two CO's and the other two metal d-orbitals are more or less non-bonding (a′). Therefore it can be expected that the four metal d-orbitals are split into two pairs. Ionizations from the two pairs of d-orbitals appear in the He(II) spectrum of Fig. 4 as bands **B** and **C** at 8.21 and 9.6 eV respectively. Their energy difference of 1.4 eV is in agreement with other d^8 Rh(I) square planar complexes [13].

Metal d-orbitals are usually split by metal–ligand interactions, which can in principal occur via σ-bonding and π-backbonding.

The σ-bonding of the monoanionic [pyrrole-2-CH=N′–t-Bu]$^-$ formed by a simple H abstraction takes place by one donative bond between the imine N′ atom and Rh and one covalent band between Rh and pyrrole N atom. The former bond length is normally about 0.1 Å longer [12, 24]. These σ donations involve the empty $d_{x^2-y^2}$ orbital.

The π-backbonding from the metal towards the ligand can be expected to be weak because [pyrrole-2-CH=N′–t-Bu]$^-$ anion does not possess a low-lying π^* orbital, since it has hardly any conjugation between its pyrrole ring and the imine group (MNDO m.o. calculations, *vide infra*). Other arguments for the absence of such a low-lying π^* orbital are the electronic transitions which take place below $\lambda < 400$ nm. As a result of the lone pair interaction the ionizations from both $n_{N'}$ and $\pi_{C=N'}$ are stabilized on going from the free ligand Hpyrrole-2-CH=N′–t-Bu to the chelate form in the Rh complex.

Going from Rh to Ir a normal consistent change is observed [13]. Figure 5 shows a much more structured spectrum than does Fig. 4. Five separate bands (**A**–**E**) are seen in the expanded (low region) UP spectra (Fig. 6). Bands **B**–**E** clearly possess a higher cross section in He(II) then in the He(I) spectrum compared to band **A**.

This latter band (**A**) is again assigned to the first π orbital of the pyrrole unit of the ligand. The IE value of $\pi(a_2)$ is 0.32 eV higher than the Rh complex as a result of the higher electronegativity of Ir. The corresponding π (b_1) ionizations of the pyrrole unit of the ligand can be observed as band **C** at 8.40 eV.

Band **B** is assigned to the highest filled Ir 5d orbital a″. The other three occupied d-orbitals of Ir are found in the He(II) spectra of Figs. 5 and 6. Ionizations from these orbitals (a′, a″, a″) give rise to the bands **C**, **D** and **E** respectively. Ionizations from 5σ, 4σ and 1π orbitals of the carbonyl groups and σ orbitals of the ligand are found at higher IE and are responsible for the overlapping region above 12 eV.

Correlation between UP Data and m.o. Calculations

The results of m.o. calculations on Hpyrrole-2-CH=N′–H (*trans* conformation) calculated by use of MNDO [25] are summarized in Table II. Molecular orbital plots of the upper four m.o.s calculated for this model ligand by MNDO are shown in Fig. 7.

The calculated m.o. characters and eigenvalues are in full agreement with the assignment of the UP spectra, as can be concluded from Table II.

With these m.o.s in mind we also performed CNDO/S m.o. calculations on the model complex [(pyrrole-2-CH=N′–H)Co(CO)$_2$] [26]. Results of these performances are also listed in Table II. Very little π-backbonding occurs from the metal towards the imine ligand, as observed by van Dam *et al.* [13].

TABLE II. Results of Semi-Empirical Molecular Orbitals Calculations on the Ligand Hpyrrole-2-CH=N'–H (a) MNDO and on the Model Complex [(Pyrrole-2-CH=N'–H)Co(CO)$_2$] (b) CNDO/S)

(a) Hpyrrole-2-CH=N'–H (*trans*)

m.o.	ϵ_i (eV)	Character	Exp IE [16]
18	−8.53	$\pi(a_2)$	7.90
17	−9.56	$\pi(b_1)$	9.00
16	−10.82	l.p. N'	9.71
15	−12.06	$\pi_{C=N'}$	10.53

Final geometry: C–N (pyrrole ring), 1.40 Å; C–C (pyrrole ring), 1.41 Å; N–H (pyrrole ring), 0.99 Å; C–H, 1.08 Å; C_2–C(pyrrole-2-to-C=N), 1.46 Å; C=N (imine part), 1.29 Å

(b) [(Pyrrole-2-CH=N'–H)Co(CO)$_2$]

m.o.	ϵ_i (eV)	Character
32	−8.13	$\pi(a_2) + p_z(N')$
31	−8.92	$\pi(b_1)$
30	−9.68	d_{xy} (74%)
29	−10.62	d_{xz} (90%)
28	−10.64	d_{z^2} (76%)
27	−10.76	σ_{Co-N}(35%) + $\sigma_{Co-N'}$ (30%)
26	−10.83	d_{yz} (90%)
25	−11.65	σ_{CO}
24	−12.26	π(40%) + $\pi_{CN'}$ (51%)
23	−12.95	π_{CO}
22	−13.78	$\sigma_{pyrrole}$
21	−14.20	$\sigma_{pyrrole}$
20	−14.50	σ_{CO}
19	−15.89	$\pi(a_1) + \pi_{CN'}$

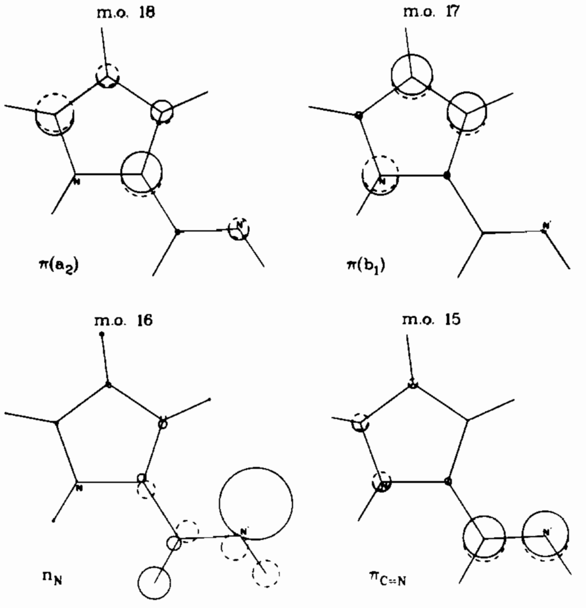

Fig. 7. Four m.o.s calculated by MNDO for Hpyrrole-2-CH=N'–H constructed from the eigenvectors.

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