Journal of Organometallic Chemistry, 289 (1985) 417–424
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A UV PHOTOELECTRONIC SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURES OF SOME COBALT AND RHODIUM "HALF SANDWICH" COMPLEXES

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(Received January 2nd, 1985)

Summary

Gas-phase He(I) and He(II) photoelectron spectra of the complexes (η-C_5H_5)M(PMe_3)X (M = Co, Rh; X = CO, CS) and (η-C_5Me_5)Rh(PMe_3)CO are reported and discussed in terms of energy sequence and composition of the valence molecular orbitals. Differences between cobalt and rhodium in bonding to the ligands are observed, rhodium interacting more strongly with the orbitals of the cyclopentadienyl ring, but being less involved in π-back donation to the empty π^* levels of the PMe_3 and X ligands. The commonly accepted opinion that CS is a better σ-donor and π-acceptor than CO is consistent with the spectroscopic data. Differences in reactivity between the "half sandwich" complexes (η-C_5R_5)ML_2 (L = CO, PR_3) are related to the observed trends in ionization energies of the HOMO.

Introduction

Gas phase UV photoelectron spectroscopy (UPS) has proved an invaluable tool in studying the nature of the bonding interactions between the central metals and the ligands in organometallic compounds. This aspect of the UPS technique has been especially used in determining the electronic structures of "sandwich" compounds [1], mainly cyclopentadienides of transition metals. Much less attention has been devoted to the investigation by photoelectron spectroscopy of "half-sandwich" complexes, although a few examples are known [2–11]. In this class of molecules the central metal is bonded to just one carbocyclic ring, other ligands, either inorganic or organic, being present. In the framework of an extensive work on the synthesis and the reactivity of low-valent transition metal "half sandwich" complexes [12,13],

0022-328X/85/$03.30

TABLE 1

IONIZATION ENERGIES (eV) OF SOME "HALF-SANDWICH" COMPLEXES OF COBALT AND RHODIUM [a]

Band lable	(η-C_5H_5)Co(PMe_3)CO (1)	(η-C_5H_5)Co(PMe_3)CS (2)	(η-C_5H_5)Rh(PMe_3)CO (3)	(η-C_5H_5)Rh(PMe_3)CS (4)	(η-C_5Me_5)Rh(PMe_3)CO (5)
	IE (eV)				
a	6.39		6.68	6.63	6.05
		6.68			
b	6.66		7.55	7.52	7.20
c	7.25	7.36			
			8.52	8.32	
d	8.04	8.04			7.83
	8.90		8.98	8.66	
		8.83			
e	(9.13)		9.58	9.39	8.73
f	10.08	10.01	10.71	10.49	10.14
		(10.51)			

[a] Values in parentheses: shoulders.

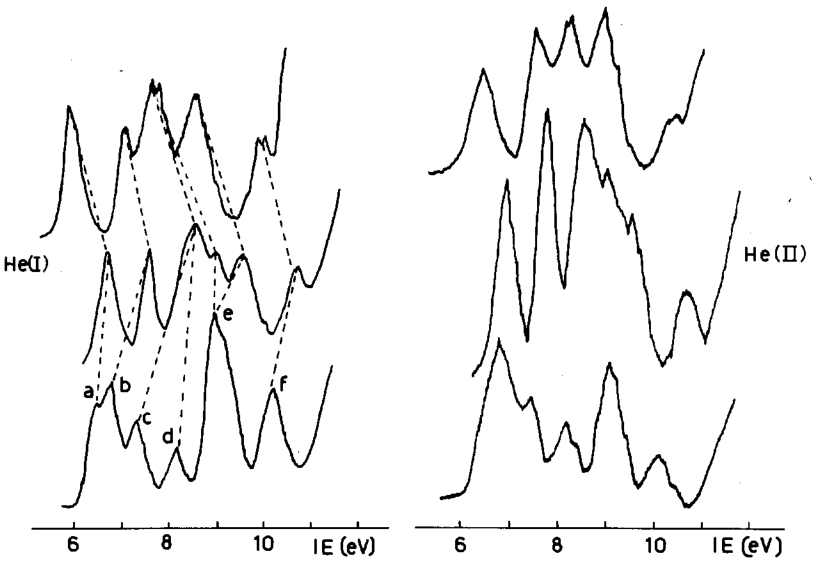

Fig. 1. Gas-phase UP spectra of (from bottom to top) (η-C_5H_5)Co(PMe_3)CO (1), (η-C_5H_5)Rh(PMe_3)CO (3), (η-C_5Me_5)Rh(PMe_3)CO (5).

we determined the UPS of the following compounds:

(η-C_5H_5)M(PMe_3)X M = Co; X = CO (**1**)
M = Co; X = CS (**2**)
M = Rh; X = CO (**3**)
M = Rh; X = CS (**4**)
(η-C_5Me_5)M(PMe_3)X M = Rh; X = CO (**5**)

The aim was not only to obtain a reliable picture of the electronic structure of these molecules, but also to get an insight into intrinsic properties of the ligands, i.e. the donor/acceptor ability of the X ligands towards the metals, the coordinating ability of the metals M, and the possible variations on going from cobalt to rhodium.

Results and Discussion

The He(I) and He(II) spectra of the above compounds are displayed in Figs. 1 and 2, and the measured ionization energies (IEs) are listed in Table 1 [14].

Assignment of the UP spectra

(η-C_5H_5)Co(PMe_3)CO (1). The electronic structure of (η-C_5H_5)Co$(CO)_2$ has been studied theoretically [15,16] and also experimentally by UPS [9,11], and accurate molecular orbital diagrams for this molecule have been presented. In terms of these models the four highest occupied levels are, in order of decreasing energy: (a) A b_1 MO arising from the bonding interaction between one of the $e^\star$ orbitals of the (η-C_5H_5)Co fragment, (Fig. 3) and a $\pi^\star$ orbital of the CO molecules. (b) An a_1 level which retains in the complex almost pure d orbital character (with a very little

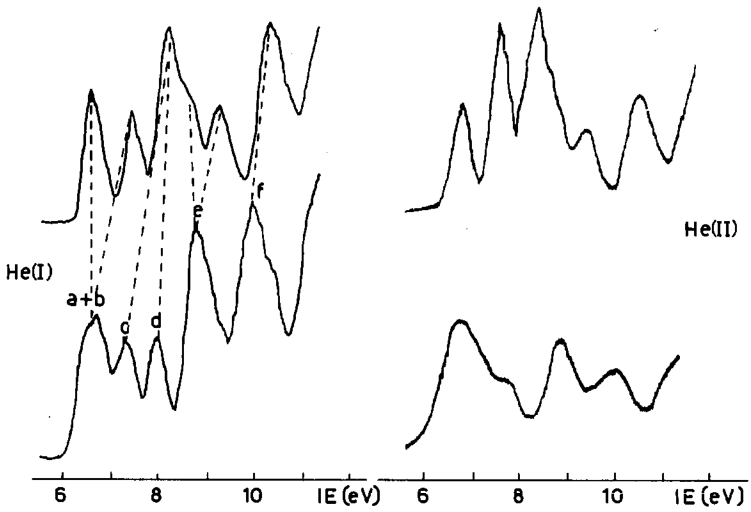

Fig. 2. Gas-phase UP spectra of (from bottom to top) (η-C_5H_5)Co(PMe_3)CS (**2**), (η-C_5H_5)Rh(PMe_3)CS (**4**).

admixture of the π orbitals of the cyclopentadienyl ring and no admixture of CO orbitals). (c) An a_1 MO representing the bonding combination of a pure cobalt d orbital and a CO π^* orbital (thus with no contribution from C_5H_5). (d) An a_2 MO arising from the interaction between one of the e_2 orbitals of the (η-C_5H_5)Co moiety and another CO π^* orbital.

Two orbitals of b_1 and b_2 symmetry follow, which correspond to the e_1 orbital of the "half-sandwich" fragment, not interacting with CO orbitals and slightly split because of differential interactions with the d metal levels, as expected in the light of an observed ring distorsion in the permethylated analogue [17]. The replacement of a CO by a PMe_3 ligand should not cause important changes in the sequence of these orbitals, since both ligand molecules possess empty π^* orbitals (in PMe_3 of predominant P $3d$ character) whilst affecting in similar ways the absolute energy values due to different inductive effects.

In the light of the above considerations, the assignment of the UP spectrum of **1** (Fig. 1) is straightforward, bands **a**–**d** being related to the four highest metal-based MOs and band **e**, with main peak at 8.90 and shoulder at 9.13 eV, to the two levels mainly localised on the cyclopentadienyl ring (e_1 in (η-C_5H_5)Co). Band **f**, at 10.05 eV, clearly arises from the ionization from the σ Co–P bonding orbital; in the UP spectrum of PMe_3 the phosphorus lone pair gives rise to a band at 8.62 eV [18], and a shift of 1.43 eV to higher IE in the complex is consistent with the formation of a σ bond. Bands **a**–**d** are shifted by approximately 1.2 eV to lower IE with respect to (η-C_5H_5)Co$(CO)_2$, band **e** by 1 eV, due to the higher electron releasing ability of PMe_3 with respect to CO.

Comparison between the He(I) and He(II) spectra supports the above assignment. Thus in the He(II) spectrum bands **a**–**d** increase in intensity relatively to band **e**, which is consistent with the substantial d nature of the orbitals to which they are related. Furthermore, band **b**, associated with the MO with the largest d character (and involving only a small contribution from the cyclopentadienyl orbitals) seems

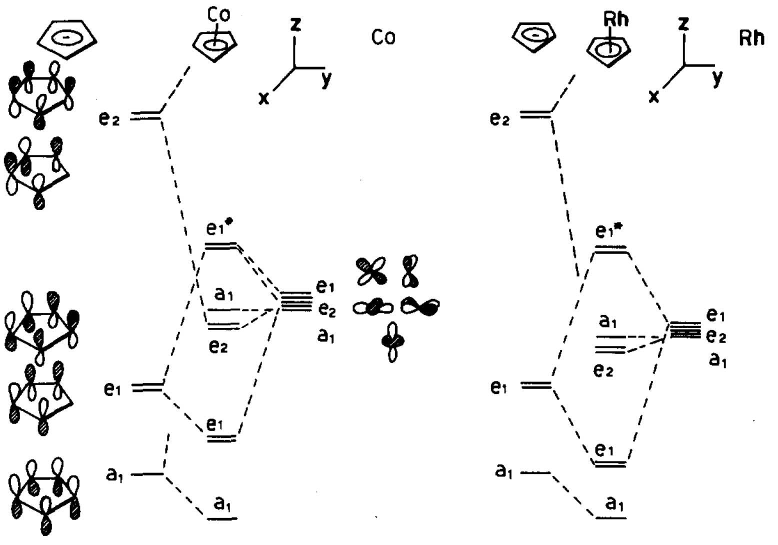

Fig. 3. Qualitative orbital interaction diagrams for the (η-C_5H_5)Co and (η-C_5H_5)Rh fragments.

to display the largest increase in intensity on passing from He(I) to He(II).

(η-C_5H_5)Co(PMe_3)CS (2). The spectrum of this compound (Fig. 2) looks very similar to that one of the analogous derivative with CO in place of CS, the most significant differences being a lower resolution (bands **a** and **b** are no longer resolved) and the presence of a shoulder on the high-energy side of band **f** (at 10.51 eV), arising from ionization from an orbital of the CS group, probably of σ nature [19]. The changes of the spectra on changing from He(I) to He(II) are similar for the two derivatives. The assignment is therefore completely analogous.

(η-C_5H_5)Rh(PMe_3)CO (3). On passing from cobalt to rhodium as coordinated metal a substantial difference is observed in the UP spectra. This is very evident in Fig. 1, where the spectra of both metal complexes with X = CO are shown.

To explain such important differences we must refer again to the electronic structure of the (η-C_5H_5)M fragments, represented in Fig. 3. When M = Rh, the d levels of the metal are closer in energy to the e_1 level of the cyclopentadienyl ring, and consequently the interaction is stronger, leading to a larger destabilization of the $e_1^\star$ and a parallel stabilization of the e_1 MO in (η-C_5H_5)Rh with respect to (η-C_5H_5)Co. Thus in the two complexes the HOMOs, derived from the $e_1^\star$ MO after a further interaction with an empty π orbital of the other ligands, are comparable in energy. This situation is reflected in the UP spectra, where band **a**, associated with the HOMO, falls at approximately the same IE in **1** and **3**. Band **b**, on the contrary, is at higher IE in **3**, consistently with the almost pure d nature of the orbital to which it is related. The assignment of the next three bands is not straightforward, but the above considerations may be of some help. Band **e** is expected to be shifted to higher IE on going from the cobalt to the rhodium complex, as a consequence of the stabilization of the e_1 level in the (η-C_5H_5)Rh fragment. The spectral region beyond 8.9 eV shows two peaks, at 8.94 and 9.56 eV, with intensities of the same order of magnitude as bands **a** and **b**, which are likely to be the analogues of band **e**. A larger splitting between the two components of this band, i.e. the two levels derived by the e_1 orbital of the (η-C_5H_5)M fragment, in the rhodium with respect to the cobalt derivative (0.60 versus 0.23 eV) was previously observed in the complexes (η-C_5R_5)M$(CO)_2$ (R = H, Me) [10,11]. The band at 8.50 eV, more intense than the others, must correspond to bands **c** and **d**, no longer resolved, the band at 10.68 eV corresponds to band **f**, related to the σ(Rh–P) orbital. This level is 0.57 eV lower than in the cobalt complex, as expected for a heavier element. The He(II) spectrum is not of great help in this case, since in the complexes of the second row transition elements the relative enhancement of the photoionization cross section of the *d* orbitals is less pronounced than in those of the first row [20]. However, the relative increase in intensity of band **d** in He(II) supports its assignment as arising from ionization from an almost pure *d* level.

*(η-C_5H_5)Rh(PMe_3)CS (**4**).* The spectrum of this complex (Fig. 2), which is very similar to that one of the analogous CO derivative, shows no unusual features and the assignment follows the same lines as those for the carbonyl compound.

*(η-C_5Me_5)Rh(PMe_3)CO (**5**).* In the permethylated complexes a destabilization of all the MOs is expected, particularly pronounced in those with predominant contribution from the rings. The analysis of the UP spectra (Fig. 1) of this complex suggests that such a differential destabilization, due to the electron-releasing ability of the methyl groups of the ring, leads to an overlapping of the component at lower IE of band **e** with band (**c** + **d**), accounting also for ionization out of two *d* metal orbitals. The result is the intense third band, with a peak at 7.83 eV, which on going from He(I) to He(II) decreases in intensity more than the two neighbouring bands. This is consistent with the contribution to this band of an ionization from a cyclopentadienyl-based orbital. Comparison between the measured IEs in **3** and **5** (Table 1) indicates that bands **b** and **f** are somewhat less affected by the inductive effects of methyls than the others; this is because they refer to MO's involving no participation by cyclopentadienyl orbitals.

General comments

From the above discussion of the experimental findings some generalizations can be made about this class of "half-sandwich" complexes. The most obvious feature is the undoubted difference in bonding behaviour between cobalt and rhodium towards the ligands. The 4*d* element seems to interact more strongly with the π orbitals of the cyclopentadienyl ring, whilst being less involved in π-back donation to the empty π^* levels of the PMe_3 and X ligands. This behaviour is consistent with a decreasing ability of the elements to form π bonds on going down a Group, while the bonding between the *d* metal and the cyclopentadienyl orbitals, of σ nature, is favoured by the better energy-matching in the rhodium complexes.

Such large differences in the UP spectra of "half-sandwich" complexes for M = Co and M = Rh had been previously observed in compounds of formula (η-C_5R_5)M$(Co)_2$ (R = H, Me) [10,11] and ascribed to excited-state effects in the positive ions, associated with electron relaxation [11].

Another interesting aspect, which in the past has received considerable attention, is the comparison between the donor/acceptor properties of the ligands X. In particular, various studies, theoretical and experimental, have been made of the electronic effects of CO and CS ligands in transition-metal complexes [21], and all reached the conclusion that CS is better σ-donor and π-acceptor than CO. This is consistent with our results, which indicate no significant difference in the electronic distribution between the carbonyl and the thiocarbonyl complexes (the IEs are practically identical for analogous compounds with X = CO and X = CS, see Table 1). The better σ-repelling ability of CS, which should induce a higher electron density on the metal, is therefore compensated by the formation of a stronger π back-bonding. For pentamethylcyclopentadienylcobalt complexes of the general type (η-C_5Me_5)CoL_2 it has been noted [9] that a progressive decrease in the first ionization energy is observed as carbon monoxide is replaced by phosphine. The corresponding values for (η-C_5Me_5)$Co(CO)_2$ and (η-C_5Me_5)$Co(PMe_3)CO$ are 6.94 and 5.99 eV, respectively [9]. The same feature is found on comparing the first IEs of (η-C_5Me_5)$Rh(CO)_2$ (6.84 eV [10]) and **5** (6.05 eV) as well as those of (η-C_5H_5)$Rh(CO)_2$ (7.64 eV [11]) and **3** (6.68 eV). The significant difference in the IE values (i.e., the energy of the HOMOs) between (η-C_5R_5)$Rh(CO)_2$ (R = H, Me) and **3**, **5** is compatible with the fact that the carbonylphosphine complexes can be readily protonated to form stable cations $[(\eta\text{-}C_5R_5)RhH(CO)PMe_3]^+$ [22,23], whereas the corresponding species $[(\eta\text{-}C_5R_5(RhH(CO)_2]^+$ are much more labile [24]. There is a general rule [13] that metal basicity of "half-sandwich" complexes (η-C_5R_5)ML_2 increases upon stepwise substitution of CO by PR_3, thus making the metal more electron-rich, and finally more ready to form a cation.

Experimental

The compounds **1** [25], **2** [26], **3** [23], **4** [26] and **5** [22] were prepared by previously described methods.

The UP spectra were recorded on a Perkin–Elmer PS 18 spectrometer equipped with a dual He(I)/He(II) source (Helectros development), at temperatures between 50 and 90°C. Calibration was performed using CH_3I, Ar and self-ionizing He as internal standard.

Acknowledgements

Thanks are due to Drs. L. Hofmann, O. Kolb and B. Klingert for providing samples of the "half-sandwich" complexes. This work was supported by the Deutsche Forschungsgemeinschaft and the Consiglio Nazionale delle Ricerche, Italy.

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