

## Ultraviolet Photoelectron Spectra of 4-Substituted Pyridine–Pentacarbonylchromium Complexes

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*The ultraviolet photoelectron spectra of  $\text{Cr}(\text{CO})_5$ -(4-RPyr) have been measured, and the IP's observed below 12 eV are discussed. Bands found in the region 7–8 eV are assigned to ionization from the chromium d orbitals. The IP values are shown to increase with the increasing electron acceptor nature of the ring substituents. The remaining bands below 12 eV are assigned to the pyridine orbitals. The IP values of the uncomplexed pyridines are observed to increase upon complexation, and a comparison is made of the effects of complexation with the  $\text{Cr}(\text{CO})_5$  and  $\text{BH}_3$  moieties.*

### Introduction

During the last few years ultraviolet photoelectron spectroscopy (pes) has become an important tool for studying the electronic behavior of those transition metal carbonyl complexes sufficiently volatile to study in the vapor phase [1]. As a continuation of our previous work on the pes of pyridine–borane complexes [2], we have prepared a series of pentacarbonyl-pyridinechromium complexes,  $\text{Cr}(\text{CO})_5(4\text{-RPyr})$ , containing various substituents on the 4-position of the pyridine ring, and we have measured their pes. A comparison of the IP values obtained for the two series of complexes yielded some interesting observations, and demonstrates the utility of the pyridine ligand system in providing a potential  $\pi$  bonding capacity with the Lewis acid, but perhaps only realizing this capacity in some excited or cationic state. The carbonyl complexes were easily prepared (in low yield though) and could readily be handled and analyzed. Most of the compounds were sufficiently stable in the vapor phase to obtain good quality spectra. The spectra of the 4-halo derivatives showed evidence of decomposition to the halopyridine and  $\text{Cr}(\text{CO})_6$  while the 4-acetyl derivative decomposed to such an extent in the spectrometer that only the first two IP's are of value.

The pes of some  $\text{Cr}(\text{CO})_5\text{L}$  complexes (L =  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{NMe}_3$ ,  $\text{PMe}_3$ ) have been reported earlier by Lloyd [3], and assignments useful to the present study were made. In the region of the spectra below

TABLE I. Vertical Ionization Potentials<sup>a</sup> of  $\text{Cr}(\text{CO})_5(4\text{-RPyr})$ .

R	IP <sub>1</sub> <sup>b</sup>	IP <sub>2</sub> <sup>b</sup>	IP <sub>3</sub>	IP <sub>4</sub>	IP <sub>5</sub>
CH <sub>3</sub> O	7.18	7.45	9.5	9.9	10.3
(CH <sub>3</sub> ) <sub>3</sub> C	7.17	7.47	10.17 <sup>c</sup>	10.57	11.2 <sup>d,e</sup>
CH <sub>3</sub>	7.22	7.48	10.21 <sup>c</sup>	10.70	11.24 <sup>d</sup>
H	7.30	7.59	10.30 <sup>c</sup>	–	11.36 <sup>d</sup>
Br	7.37	7.64	10.35 <sup>f</sup>	–	–
Cl	7.42	7.66	10.6 <sup>f</sup>	–	–
CH <sub>3</sub> CO	7.5	7.8	–	–	–

<sup>a</sup>In eV. <sup>b</sup>Assigned to the chromium d orbitals – see text. <sup>c</sup>Assigned to the ring a<sub>2</sub> orbital – see text. <sup>d</sup>Tentatively assigned to the ring b<sub>1</sub> orbital – see text. <sup>e</sup>Shoulder. <sup>f</sup>Center of broad band with shoulder on high energy side. Additional bands at 12.18 eV (chloro compound) and 11.42 eV (bromo compound) assigned to the halogen lone pair.

12 eV, the observed bands are due to ionization from orbitals largely on the chromium or the ring, with no apparent interference from orbitals predominantly CO in character.

### Results and Discussion

The IP values below 12 eV are listed in Table I. The C<sub>4v</sub> site symmetry about the chromium in complexes of the form  $\text{Cr}(\text{CO})_5\text{L}$  results in a splitting of the filled t<sub>2g</sub> orbitals into e and b<sub>2</sub> components. In the spectra of the pyridine complexes the result is two clearly resolved IP's (IP<sub>1</sub>, IP<sub>2</sub>). The first peak is somewhat dominant and is probably due to ionization from the e orbital, in accordance with the assignment of Lloyd [3].

The values for the d orbitals may be compared with the value of 8.4 eV found for  $\text{Cr}(\text{CO})_6$  [4], and this represents a significant lowering. In fact, with the exception of the 4-acetyl derivative, the values obtained in this work are lower than the values obtained for  $\text{Cr}(\text{CO})_5\text{NMe}_3$  (7.45 eV and 7.76 eV for the e and b<sub>2</sub> orbitals [3]), while the magnitude of the e–b<sub>2</sub> splitting is comparable to that of the  $\text{NMe}_3$  compound. Thus substitution of one CO by a pyridi-

TABLE II. Vertical Ionization Potentials<sup>a</sup> of 4-Substituted Pyridine-Boranes<sup>b</sup>.

Substituent	IP <sub>1</sub>	IP <sub>2</sub> <sup>c</sup>	IP <sub>3</sub> <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> C	9.45	10.30	11.21
CH <sub>3</sub>	9.50	10.45	11.41
H	9.72	10.63	11.88
Cl	9.71	10.84	11.37 <sup>e</sup>
Br	9.71	10.82	11.07 <sup>e</sup>

<sup>a</sup>In eV. <sup>b</sup>Data taken from reference 2. Additional data and annotation included in reference 2. <sup>c</sup>Ring a<sub>2</sub> orbital. <sup>d</sup>Assigned to b<sub>1</sub> orbital. <sup>e</sup>Significant admixture of halogen lone pair character.

ne ligand results in a significant increase in the amount of electronic charge placed at the chromium. Both IP's correlate smoothly with the  $\sigma_p$  values of the substituents [5],  $IP_1 = 0.442\sigma_p + 7.29$ , and  $IP_2 = 0.446\sigma_p + 7.56$ . No IP value was more than 0.03 eV from the regression line. The lack of deviation from the standard  $\sigma_p$  correlation, and particularly the lack of any enhanced effect of the methoxy substituent, argues against any resonance interaction between the correlations involving the e and b<sub>2</sub> orbitals indicates substituents and the chromium. The similarity in slope between the unimportance of any interaction which would discriminate between these orbitals. This would be true in the ground state as well as in the cation produced by the loss of a d electron. Thus the  $\sigma$ -only model for pyridine liganacy [6-8] seems to be supported in this study, wherein the effect of the increased donor nature of the substituents on the d orbital ionization energies is merely to provide increasing electron density at the chromium. Certainly no evidence is presented here for the behavior of the pyridine system as a  $\pi$  backbonding ligand.

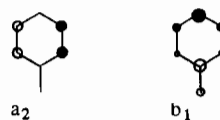
The first IP in the spectra of the substituted pyridine-boranes, 4-RPyr·BH<sub>3</sub> (Table II contains selected data), is due to the group orbitals of the BH<sub>3</sub> [2]. The IP<sub>1</sub> values correlated with the  $\sigma_p$  values of the ring substituents, giving rise to two regression lines,  $IP = 1.52\sigma_p + 9.73$  for electron donor substituents, and  $IP = 1.02\sigma_p + 9.48$  for electron withdrawing substituents. The BH<sub>3</sub> group orbitals are then significantly more sensitive to the nature of the ring substituents than the chromium d orbitals, and apparently more sensitive therefore to changes in electron density at the donor-acceptor bond.

Three IP's attributed to the pyridine ring are considered to be present below 12 eV in the pes of pyridine compounds (Table III). These are due to the a<sub>1</sub> orbital which contains significant nitrogen lone pair character, and the a<sub>2</sub> and b<sub>1</sub>  $\pi$  orbitals [9] (the latter may contain substituent orbital character in many 4-substituted derivatives). The ionization from the a<sub>1</sub> orbital is sometimes poorly separated from one of the

TABLE III. Vertical Ionization Potentials<sup>a</sup> of 4-Substituted Pyridines.

Substituent	IP <sub>1</sub>	IP <sub>2</sub> <sup>b</sup>	IP <sub>3</sub> <sup>c</sup>
H <sup>d</sup>	9.60 <sup>e</sup>	9.75	10.50
CH <sub>3</sub> <sup>d</sup>	9.50 <sup>e</sup>	9.60	10.05
(CH <sub>3</sub> ) <sub>3</sub> C <sup>d</sup>	9.3 <sup>e</sup>	9.5	9.7
Cl	10.2 <sup>f</sup>		

<sup>a</sup>In eV. <sup>b</sup>Assigned to the a<sub>2</sub> orbital. <sup>c</sup>Assigned to the b<sub>1</sub> orbital. <sup>d</sup>See reference 9. <sup>e</sup>Shoulder or overlapping band. <sup>f</sup>Center of broad band.



other two peaks [10], and in the study on pyridine-boranes, the band due to the a<sub>1</sub> orbital (B-N bonding) was not assigned [2]. In the present study, two and sometimes three peaks are observed in the region 9-12 eV, and although some assignments appear straightforward, others remain ambiguous.

The first of these bands (IP<sub>3</sub>) in the spectrum of the unsubstituted pyridine complex, as well as the methyl and t-butyl substituted complexes, is due to the a<sub>2</sub>  $\pi$  orbital. The increase in the a<sub>2</sub> IP value upon complexation of the pyridine is 0.6-0.7 eV (Tables I and III), which compares with the 0.5-0.6 eV increase found for N-oxide formation [11], and is slightly less than the 0.8-0.9 eV found for borane complex formation [2].

The other possibility for IP<sub>3</sub>, assignment to the a<sub>1</sub> orbital, is quite unlikely, since this would mean that upon complexation the a<sub>1</sub> orbital, which is directly involved in the donor-acceptor bond, is stabilized by only 0.7-0.9 eV. This would be less than the stabilization of the other ring orbitals and far short of the 2.2 eV stabilization found by Lloyd [3] for the nitrogen lone pair of NMe<sub>3</sub>.

The presence of two remaining peaks below 12 eV in the spectra of the methyl and t-butyl complexes (IP<sub>4</sub> and IP<sub>5</sub>) presents a problem in specifying the position of the b<sub>1</sub>  $\pi$  orbital. The assignment of IP<sub>5</sub> to the b<sub>1</sub>  $\pi$  orbital appears somewhat more reasonable than its assignment to IP<sub>4</sub> since the 1 eV separation between the a<sub>2</sub> and b<sub>1</sub>  $\pi$  orbitals found for the N-oxides and borane complexes would be preserved in the chromium carbonyl complexes. More importantly if the alternative assignment were true, the stabilization of the b<sub>1</sub> orbital upon complexation of the methyl and t-butyl pyridines would be hardly more than that found for the a<sub>2</sub> orbital (Tables I and III). This would obtain despite the fact that the latter has a nodal plane through positions 1 and 4,

and should therefore be considerably less affected by complexation, as seen in the studies on N-oxide [11] and borane complex formation. It should be pointed out though that this assignment is somewhat tenuous. Moreover the implication that IP<sub>4</sub> is then due to the a<sub>1</sub> orbital is poorly founded because of the disturbing lack of such a peak at ca. 10.9 eV in the pes of the unsubstituted pyridine complex (the constant relative intensity of IP<sub>4</sub> over a number of spectra, measured on several different samples of the methyl and t-butyl complexes, would argue against attribution to an impurity).

An interesting contrast is made here with the IP's of the borane complexes (Table II). The increase in IP of the pyridine orbitals upon complexation with the Cr(CO)<sub>5</sub> group is less than upon BH<sub>3</sub> adduct formation. This appears particularly true for the b<sub>1</sub> orbital, though the effect of this phenomenon would depend on the nature of the 4-substituent if the b<sub>1</sub> IP assignments are correct. For instance the spectra of the 4-halo-pyridine-boranes show the a<sub>2</sub> and b<sub>1</sub> IP's as two identifiable peaks. In the spectra of the chromium complexes the whole band envelope is not only shifted to a lower energy, but only one broad peak is seen, with at most a poorly resolved shoulder. This seems due to the small difference in the b<sub>1</sub> IP value between the uncomplexed halopyridine and its chromium carbonyl complex, certainly no more than 0.3–0.6 eV for the chloro complex (pure 4-bromopyridine too easily self quaternizes for pes measurement). It should be pointed out that the b<sub>1</sub> orbital of the halo derivatives is not localized on the ring but contains considerable halogen character. Assuming the b<sub>1</sub> IP's in the other complexes are those given in Table I, the difference in IP values between the complexed and uncomplexed pyridines increases with the increasing donor nature of the substituent (0.9 eV upon complexation of the unsubstituted pyridine, 1.2 eV for the 4-methyl derivative, and 1.5 eV for the 4-t-butyl derivative).

Evidence is presented here, and in the work of Lloyd [3], that charge donation from amines to the Cr(CO)<sub>5</sub> exerts less of an effect on the electron energies of the ligand than charge donation to the BH<sub>3</sub> group. However an important alternative or perhaps supplementary effect might be present in the Cr(CO)<sub>5</sub>Pyr system. Recent observations of the d–d transition energies [12, 13] and C–O stretching frequencies [12, 13] in a series of complexes W(CO)<sub>5</sub>(RPyr) shows no evidence that the nature of the substituent on pyridine appreciably influences the electronic nature of the ground state of the W(CO)<sub>5</sub> group. More generally, C–O stretching force constants for M<sup>VI</sup>(CO)<sub>5</sub>(amine) complexes appear to be insensitive to the nature of the amine [14]. However Wrighton [12] has identified a W → pyridine charge-transfer transition in the electronic spectra of W(CO)<sub>5</sub>(RPyr), presumably involving the dπ orbitals

of the tungsten and the π\* orbitals of the ring. He has shown that the energy of the charge-transfer transition is quite sensitive to the nature of the ring substituent, decreasing by 0.7 eV from the 4-methylpyridine complex to the 4-acetylpyridine complex. This is due to the increased electron affinity of the ring π\* orbitals with electron withdrawing substituents. Thus, in the present study, although the pyridine π system is apparently little involved in bonding to chromium in the ground state, the cationic states produced by the loss of a pyridine π electron could be stabilized by charge-transfer from the chromium dπ orbitals. This would account for the smaller increase in pyridine IP values upon complexation, especially for the b<sub>1</sub> ring orbital. Moreover stabilization of the cation would be of decreasing importance with the more electron donating substituents on the ring, supporting the assignments made for the b<sub>1</sub> orbital. Thus symmetry allowed effects, which are deemed unimportant in determining the ground state electronic nature of substituted metal carbonyl systems, could be of increasing importance in electron deficient cationic states.

## Experimental

### Preparation of Compounds

The substituted pyridine complexes were prepared by the method of Connor [15] from the salt Et<sub>4</sub>N<sup>+</sup>[Cr(CO)<sub>5</sub>Br]<sup>−</sup>, ca. 10–20% molar excess of the substituted pyridine, and Et<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>−</sup> in methylene chloride solution at room temperature. The halide starting material was prepared by the method of Abel [16]. The complexes were purified by crystallization from hexane or petroleum ether, occasionally followed by sublimation and a recrystallization from hexane or petroleum ether. The analytical data are listed in Table IV.

TABLE IV. Analytical Data on Cr(CO)<sub>5</sub>(4-RPyr).

R	M.p., °C	% C		% H	
		Calcd.	Found	Calcd.	Found
H <sup>a</sup>	95–97°				
CH <sub>3</sub>	101–103°	46.33	46.69	2.47	2.49
(CH <sub>3</sub> ) <sub>3</sub> C	108–111°	51.38	51.39	4.00	3.94
CH <sub>3</sub> O	97–99°	43.88	44.29	2.34	2.51
Cl <sup>b</sup>	123–125°	39.30	39.16	1.32	1.36
Br	152–155°	34.31	34.63	1.15	1.24
CH <sub>3</sub> CO	98–101°	46.02	46.44	2.25	2.18

<sup>a</sup>Reference 18 gives m.p. 95–96 °C.

<sup>b</sup>Reference 19 gives

m.p. 128 °C. (dec.).

The complexes could be easily and clearly characterized by their mass spectra, since the initial fragmentation involves only the successive loss of CO groups [17] (except for the t-butyl derivative), without any interfering fragmentation. In all cases the molecular ion peaks were observed, followed by those due to the loss of CO. None of the complexes showed peaks at  $m/e$  values higher than the molecular ion. The spectra of the halo and acetyl derivatives showed appreciable amounts of  $\text{Cr}(\text{CO})_6$ , consistent with observations on their photoelectron spectra (*vide supra*), but otherwise the spectra were for the most part free of any spurious peaks. The t-butyl derivative had a somewhat more complex spectrum, in that not only did fragmentation occur with the loss of CO, but considerable fragmentation corresponded to the loss of a methyl group followed by the usual loss of CO.

#### Measurement of Photoelectron Spectra

The spectra were obtained with a Perkin-Elmer Model PS-18 photoelectron spectrometer, using the He(I) resonance line (21.22 eV). Since elevated temperatures were necessary for proper sample vapor pressures, a direct inlet probe was used for all samples. The spectra were calibrated with Ar (15.759 eV line) and Xe (12.130 eV line), used as internal standards. The IP values listed in Table I are the band maxima.

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