Inorganica Chimica Acta, 57 (1982) 195–198
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The Bonding in Some Bis(arene)Chromium Compounds as Indicated by U.V. Photoelectron Spectroscopy

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Received May 29, 1981

He(I) ultraviolet photoelectron (UV-PES) spectra are reported for several bis(arene)chromium compounds. The arenes concerned are m-*trifluoromethylbenzotrifluoride,* p-*fluorobenzotrifluoride,* p-*difluorobenzene,* m-*dichlorobenzene, fluorobenzene, chlorobenzene, methylbenzoate,* p-*chlorotoluene, diphenyl ether, toluene,* o-*xylene, trimethylsilylbenzene, isobutylbenzene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, and 1,2,4,5-tetramethylbenzene. The spectra have been interpreted using a qualitative perturbation molecular orbital model. The two major findings of the work are: (i) the ionizations from the metal-localized a_{1g} and e_{2g} molecular orbitals are governed primarily by ligand electronegativity, but there is some evidence for the operation of conjugative effects, and (ii) the ionization energies of the free and coordinated arenes are quite similar.*

Introduction

The electronic structures and reactivity patterns of sandwich molecules have attracted the attention of theoreticians and experimentalists for several years. Dibenzene chromium, the best known Group VIB sandwich molecule, has been investigated theoretically by both semi-empirical [1], *ab initio* [2] and X_α [3] molecular orbital (MO) methods. Experimental evidence bearing on the electronic structure of $(\eta^6\text{-}C_6H_6)_2Cr$ has come from *e.g.* ^{13}C NMR [4] and UV photoelectron spectroscopy [5, 6]. Apart from a ^{13}C NMR study [4], the substituted arene complexes of chromium have been investigated much less extensively. Photoelectron spectroscopic examination, for example, has been confined to two methylated derivatives [5, 6]. In part, the paucity of spectroscopic data for the cognates of dibenzene chromium stemmed from the limitations of the conventional synthetic methodology. However, the pioneering development of the metal atom synthesis of sandwich molecules by Timms [6] has made available a much wider range of aromatic substituents to refine further the bonding descriptions of sandwich molecules using He(I) UV photoelectron spectroscopy (UV-PES).

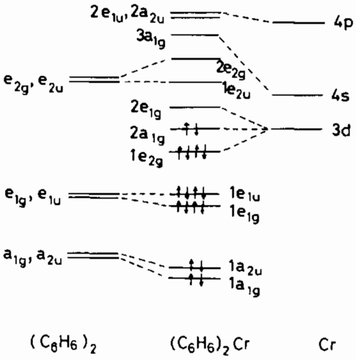

Fig. 1. A qualitative MO scheme for bis(arene)chromium complexes.

Experimental

All compounds are known and were synthesized by metal vapor synthesis techniques as described in the literature [4]. Prior to measurement of the UV-PES, all compounds were sublimed and checked by high resolution mass spectroscopy.

The spectra were acquired using a Perkin-Elmer Model PS-18 photoelectron spectrometer equipped with a He I source. All samples were introduced *via* a direct inlet heated probe system at elevated temperatures, with the temperature maintained at the minimum required to obtain reasonable spectra since each compound tended to decompose at approximately 50 °C above the sublimation temperature. A mixture of rare gases, argon (15.759 eV) and xenon (12.130 eV), was used for internal calibration of each spectrum. The resolution of the instrument was maintained at 25–50 meV with the temperature controlled to ±2 °C. All quoted ionization energies (IE's) are band maxima unless otherwise indicated.

TABLE I. Ionization Energy Data (eV) for Bis(arene)chromium Complexes.

Compound	Ionic State[a]				$\Delta^2E_{2g}/^2A_{1g}$ $(I_2 - I_1)$	$\Delta^2E_{1g}/^2E_{1u}$ $(I_4 - I_3)$
	$^2A_{1g}$ (I_1)	$^2E_{2g}$ (I_2)	$^2E_{1u}(I_3)$	$^2E_{1g}(I_4)$		
$(m\text{-}F_3CC_6H_4CF_3)_2Cr$ (*1*)	6.70	7.72	11.01 (broad)		1.02	b
$(p\text{-}FC_6H_4CF_3)_2Cr$ (*2*)	6.59	7.46	10.20	10.66	0.87	0.46
$(p\text{-}FC_6H_4F)_2Cr$ (*3*)	6.38	7.18	10.00	10.56	0.80	0.56
$(m\text{-}ClC_6H_4Cl)_2Cr$ (*4*)	6.20	7.03	9.83 (broad)		0.83	b
$(C_6H_5F)_2Cr$ (*5*)	5.91	6.71	9.85	10.15	0.80	0.30
$(C_6H_5Cl)_2Cr$ (*6*)	5.90	6.81	9.65	10.18	0.91	0.53
$(C_6H_5CO_2CH_3)_2Cr$ (*7*)	5.77	6.80	10.16 (broad)		1.03	b
$(p\text{-}ClC_6H_4CH_3)_2Cr$ (*8*)	5.76	6.70	9.31	10.03	0.94	0.72
$[(C_6H_5)_2O]_2Cr$ (*9*)	5.52	6.36	8.73	9.25	0.84	0.52
$(C_6H_6)_2Cr$ (*10*)	5.40	6.40	9.6 (broad)		1.00	b
$(CH_3C_6H_5)_2Cr$ (*11*)	5.31	6.24	9.18	9.71 (shoulder)	0.93	0.53
$(o\text{-}H_3CC_6H_4CH_3)_2Cr$ (*12*)	5.21	6.18	9.10 (broad)		0.97	b
$[C_6H_5Si(CH_3)_3]_2Cr$ (*13*)	5.22	6.32	9.59 (broad)		1.10	b
$[C_6H_5CH_2CH(CH_3)_2]_2Cr$ (*14*)	5.23	6.19	9.24	9.56	0.96	0.32
$[1,2,3\text{-}(CH_3)_3C_6H_3]_2Cr$ (*15*)	5.04	5.96	8.90	9.18 (shoulder)	0.92	0.28
$[1,3,5\text{-}(CH_3)_3C_6H_3]_2Cr$ (*16*)	4.97	5.85	8.87	9.22 (shoulder)	0.88	0.35
$[1,2,4,5\text{-}(CH_3)_4C_6H_2]_2Cr$ (*17*)	4.85	5.65	8.49	8.90	0.80	0.41

[a] Even though the substituted arenes possess lower symmetries, D_{6h} labelling of states and orbitals is used: see text. [b] Peaks I_3 and I_4 not resolved.

Results and Discussion

The Discussion can start advantageously by considering a 'back-of-the envelope' molecular orbital (MO) scheme for the parent molecule, dibenzene chromium. The symmetry of this species has been shown to be D_{6h} by both X-ray crystallography [8] and electron diffraction [9]. Pairs of the familiar π-type MO's of benzene have been symmetry adapted [10] and appear in the left hand side of Fig. 1. The D_{6h} point group effects a differentiation of the Cr(3d) AO's into symmetries e_{1g} (d_{xz}, d_{yz}), e_{2g} $(d_{xy}, d_{x^2-y^2})$, and a_{1g} (d_{z^2}). The Cr(3d) AO's then interact with the ligand π combinations according to the prescriptions of qualitative MO theory. In this manner, the metal e_{1g} MO's are destabilized and stabilized respectively, while the reverse is true for the metal and ligand MO's of e_{2g} symmetry. To a first approximation, the totally symmetric metal $2a_{1g}$ MO is non-bonding since it is stabilized by interaction with the Cr(4s) virtual orbital, and destabilized by interaction with the filled ligand $1a_{1g}$ MO.

It is appropriate at this point to make some remarks relating to Fig. 1. First, semi-empirical MO calculations [1] on $(\eta^6\text{-}C_6H_6)_2Cr$ are not in complete agreement regarding the actual sequence of MO's in the molecular ground state. However, these calculations and the x_α calculation [3] are in agreement regarding the metal-localized $2a_{1g}$ and $1e_{2g}$ MO's; they occur in the sequence shown in Fig. 1. Secondly, mention should also be made of the breakdown of Koopmans' theorem [11] for several organometallic complexes due to the substantial relaxation energies associated with electron ejection from metal-localized orbitals [12]. Thus, *ab initio* calculations [2] on $(\eta^6\text{-}C_6H_6)_2Cr$ revealed that in the molecular ground state the metal-localized e_{2g} MO is less stable than the a_{1g}. However, ΔSCF calculations on the first two ionic states indicated that much larger relaxation energies are associated with the ionization of the a_{1g} MO because of the higher percentage of metal character. Thirdly, the symmetries of the substituted $(arene)_2Cr$ species are obviously lower than D_{6h}. However, the rings can be regarded as freely rotating; moreover, additional splittings due to the lower symmetry are not discernable spectroscopically. Clearly, Fig. 1 is a very qualitative representation of the MO's of bis(arene)chromium complexes; nevertheless, it is useful for making spectroscopic assignments and delineating trends.

All the spectra, of which that of $(C_6H_5F)_2Cr$ is typical (Fig. 2), exhibit three peaks in the spectral region less than 11 eV (Table I). Using Fig. 1 and the previous assignments for dibenzene chromium [5, 6], the first (~4.9–6.7 eV) and second (~5.7–7.7 eV) peaks are assigned to the production of the $^2A_{1g}$ and $^2E_{2g}$ metal-localized states, respectively, while

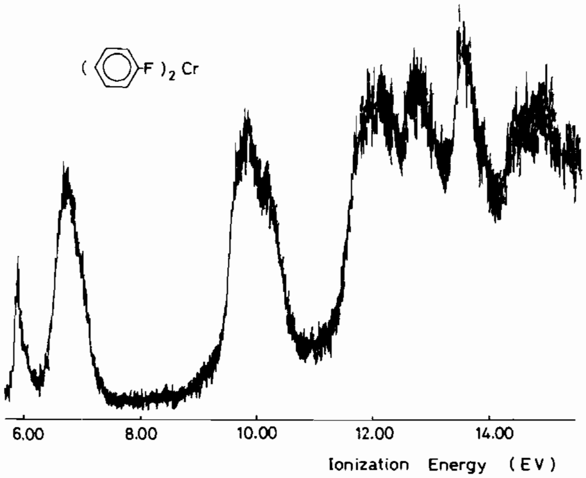

Fig. 2. He(I) ultraviolet photoelectron spectra of $(C_6H_5F)_2$-Cr.

the third peak (~8.5–11.0 eV), which sometimes exhibits perceptible splitting (*vide infra*), is assigned to electron ejections from the $1e_{1g}$ and $1e_{1u}$ ligand-centered MO's. The relative photoionization cross sections for these assignments are crudely commensurate with the relative orbital degeneracies.

As pointed out above, the $2a_{1g}$ metal-localized MO (Fig. 1) is essentially non-bonding. The only MO of the same symmetry has its origins in the arene a_{2u} π-type MO which, in free C_6H_6 has an ionization energy of 12.1 eV [13]. Since the 3d AO s of free chromium atoms have an ionization energy of 7.2 eV [14], there is a significant energy gap between the $1a_{1g}$ and $2a_{1g}$ MO's. In view of this, the $2a_{1g}$ metal-localized MO in bis(arene)chromium compounds should respond primarily to ligand electronegativity changes and only in a minor way to conjugative effects in the arene ligands. Inspection of Table I reveals that there is indeed a qualitative relationship between group electronegativities [15] of the arene substituents and the magnitude of the first IE. Note, however, that compounds *1* and *3* should be reversed on the basis of electronegativity considerations. We attribute this observation to the fact that the CF_3 group is incapable of conjugation with the arene ring. On the other hand, π-donation from F(2p) AO's destabilizes *inter alia* the lowest π-MO of arenes [16, 17]. In turn, interaction between the $1a_{1g}$

TABLE II. Ionization Energy Data (eV) for Free and Complexed Arenes.

Arene	Free '$^2E_{1g}$'[a]	Complexed $^2E_{1u}$	$^2E_{1g}$	Δ Free/Complexed
m-$F_3CC_6H_4CF_3$	10.57[b]	11.01 (broad)		0.4
p-$FC_6H_4CF_3$	9.98[b]	10.20	10.66	0.45
p-FC_6H_4	9.87[c]	10.00	10.56	0.41
m-ClC_6H_4Cl	9.55[d]	9.83 (broad)		0.3
C_6H_5F	9.46[e]	9.85	10.15	0.54
C_6H_5Cl	9.51[c]	9.65	10.18	0.40
$C_6H_5CO_2CH_3$	9.79[b]	10.16 (broad)		0.4
p-$ClC_6H_4CH_3$	9.23[c]	9.31	10.03	0.44
$(C_6H_5)_2O$	8.72[f]	8.73	9.25	0.27
C_6H_6	9.24[g]	9.6 (broad)		0.4
$CH_3C_6H_5$	8.89[e]	9.18	9.71 (shoulder)	0.47
o-$H_3CC_6H_4CH_3$	8.67[h]	9.10 (broad)		0.4
$C_6H_5Si(CH_3)_3$	9.16[i]	9.59 (broad)		0.4
$C_6H_5CH_2CH(CH_3)_2$	8.98[j]	9.24	9.56	0.42
1,2,3-$(CH_3)_3C_6H_3$	8.6 [k]	8.90	9.18 (shoulder)	0.4
1,3,5-$(CH_3)_3C_6H_3$	8.42[l]	8.87	9.22 (shoulder)	0.62
1,2,4,5-$(CH_3)_4C_6H_2$	8.13[b]	8.49	8.90	0.56

[a] See text for definition. [b] Measured in our laboratory. [c] Reference 16. [d] J. N. Murrell and R. J. Suffolk, *J. Electron Spectrosc. Relat. Phenom., 1,* 471 (1972/1973). [e] Reference 17. [f] J. H. D. Eland, *Int. J. Mass Spectron Ion Phys., 2,* 471 (1969). [g] Reference 12. [h] J. P. Maier and D. W. Turner, *J. Chem. Soc. Faraday Trans. II, 69,* 196 (1973). [i] P. K. Bischof, M. J. S. Dewar, D. W. Goodman and T. B. Jones, *J. Organomet. Chem., 82,* 89 (1974). [j] E. Nagy-Felsobuki and J. B. Peel, *J. Electron Spectrosc. Relat. Phenom., 16,* 397 (1979). [k] M. Klessinger, *Angew. Chem. Int. Ed., 11,* 515 (1972). [l] T. Koenig and M. Tuttle, *J. Org. Chem., 39,* 1308 (1974).

and $2a_{1g}$ MO's (Fig. 1) destabilizes the latter slightly. This π-donor effect is presumably also responsible for the destabilization of the $2a_{1g}$ metal-localized MO upon progressive methyl substitution.

Inspection of Table I indicates that the trends in the second IE of bis(arene)chromium complexes follow those of the first IE rather closely, hence the metal-localized $1e_{2g}$ MO also responds primarily to changes in ligand electronegativity. The differences between the first and second IE's – *i.e.* the energy differences between the $^2E_{2g}$ and $^2A_{1g}$ ionic states – provide evidence for the operation of conjugative effects in some instances. It is clear that the compounds exhibiting smaller $I_2 - I_1$ values (Table I) (~0.8–0.88 eV) are those with substituent lone pairs adjacent to the benzene ring, while those with larger energy differences (>0.91 eV) possess carbon or silicon atoms adjacent to the ring. In a previous section, it has been suggested that π-donor groups are capable of slightly destabilizing the metal-localized $2a_{1g}$ MO. In order for the gap between the $2a_{1g}$ and $1e_{2g}$ MO's to diminish, it is clear that π-donor groups must also destabilize the latter.

Attention is now turned to the third and fourth ionizations of bis(arene)chromium complexes. As implied earlier, part of the bonding in bis(arene)-chromium complexes stems from interaction between the vacant e_{1g} metal MO and an occupied arene MO of the same symmetry. For this reason, the third and fourth ionizations (Table I and Fig. 1) are assigned to the production of $^2E_{1u}$ and $^2E_{1g}$ ionic states, respectively. (Note that in some instances the third and fourth ionizations are overlapping). In Table II the energies of the $^2E_{1g}$ state in the free arenes are compared with those in the corresponding bis(arene)-chromium complexes. Note that some simplifying assumptions have been made regarding the comparisons in Table II. For example, in monosubstituted benzenes (C_{2v} symmetry), the e_{1g} MO splits into a_2 and b_1 MO's, the latter being destabilized by interaction with π-donor groups [16, 17]. In Table II, therefore, we have taken the mean of the published $^2A_2$ and $^2B_1$ ionic states to be the energy of the '$^2E_{1g}$' state. Interestingly, the stabilization of the HOMO of the arene upon complexation – *i.e.* the difference between the energy of the $^2E_{1g}$ state in the free and complexed ligand – is rather constant and in the range 0.3–0.6 eV. In fact, the photoelectron spectra of the free and complexed arenes are generally quite similar from 9 eV upward.

One final interesting feature of the UV-PES data for dibenzene chromium and its cognates is the fact that the first IE of $[1,2,4,5\text{-}(CH_3)_4C_6H_2]_2Cr$ (4.85 eV) is, to our knowledge, the smallest value reported for a transition metal compound. Undoubtedly, this factor is responsible for the ease of oxidation of bis-(arene)chromium compounds.

Acknowledgments

The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612) and the Robert A. Welch Foundation for generous financial support. Gratitude is also expressed to R. Bard, R. Harris, V. Graves and T. Lenert for synthesizing the compounds used in this work.

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