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Temporary Anion States of π-Ligand Transition-Metal Carbonyls Studied by means of Electron Transmission Spectroscopy and Xα Calculations

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Abstract: The resonances observed in the electron transmission spectra of (benzene)chromium tricarbonyl, (cyclopentadienyl)manganese tricarbonyl, (1,3-butadiene)iron tricarbonyl, and (cyclopentadienyl)cobalt dicarbonyl have been assigned with the aid of MS Xα calculations. In contrast with previous theoretical results, the present calculations on the neutral states show a large net electronic charge transfer from the π ligand to the metal.

The valence occupied molecular orbitals (MOs) of transition-metal complexes have been extensively characterized in energy and nature by UV photoelectron spectroscopy and theoretical studies. The complementary information on the vacant energy levels, however, is very scarce.

Electron transmission spectroscopy (ETS)[1] is one of the most powerful means for the determination of gas-phase electron affinities (EAs). This electron scattering technique takes advantage of the sharp variations in the total electron scattering cross section caused by resonance processes to measure the energies at which temporary electron capture into normally unoccupied MOs occurs. These attachment energies (AEs) are the negative of the EAs, and, in a Koopmans' theorem sense, they can be associated with the energies of the empty MOs.

ETS has long been used to study atoms and small molecules and, more recently, has been applied to organic systems.[2] Only a few applications of ETS to transition-metal complexes, such as hexacarbonyls,[3] first-row transition metallocenes,[4,5] and bis(benzene)chromium,[6] have appeared. In the present paper, we extend our ETS study of prototype transition-metal complexes to d^6 and d^8 arene carbonyl complexes, such as (benzene)chromium tricarbonyl, (cyclopentadienyl)manganese tricarbonyl, (1,3-butadiene)iron tricarbonyl, and (cyclopentadienyl)cobalt dicarbonyl, including the methyl and methoxy derivatives of the chromium complex.

The assignment of the resonances observed in our earlier ETS studies on metallocenes[5] and bis(benzene)chromium[6] was supported by MS–Xα calculations, which accurately reproduced the experimental AEs. We employ the same computational method also in the present study, where the lower symmetry of the complexes allows for a large mixing between the metal and ligand fragment orbitals and prevents a simple qualitative characterization of the anion states.

Experimental and Computational Methods

Our electron transmission apparatus is in the format devised by Sanche and Schulz[1] and has been previously described.[7] A magnetically collimated electron beam is selected in energy by a trochoidal monochromator[8] and passed through a gas-filled collision chamber. A retarding voltage is responsible for the rejection of those scattered electrons which have lost a given amount of axial velocity. Resonance processes take place over a narrow energy range. To enhance the variations in the total scattering cross section, in correspondence with the formation of temporary anion states, the impact energy of the electron beam is modulated with a small ac voltage and the first derivative of the transmitted current is detected by using a synchronous lock-in amplifier.

The apparatus can be operated[9] in such a mode so as to detect the nearly total scattering cross section (high rejection) or the differential backscattering cross section (low rejection). Here the high-rejection spectra are reported.

The AEs given correspond to the vertical midpoints between the minima and the maxima of the differentiated signal. The $(1s2s^2)$ ^2S anion state of helium was used for calibration of the energy scales, and the estimated accuracy of the reported AEs is ±0.05 or ±0.1 eV, depending upon the number of decimal places quoted.

Multiple scattering Xα calculations were performed on the metal complexes at their experimental geometries[10] following the procedure described in ref. 6. The atomic sphere radii satisfying the virial ratio $(-2T/V = 1)$ for the neutral complexes are reported in Table I and were also used for the ionic states.

The ionization energies (IEs) and AEs were evaluated by using Slater's transition-state method[11] and hence include relaxation effects, which strongly influence the ordering of anion and cation states in metal complexes.

The charge distributions in the neutral molecules were computed by partitioning the intersphere and outersphere charges among the atoms according to the procedure of Case and Karplus,[12] thus avoiding the approximation of attributing all the charge in these regions to the ligands. The MS–Xα calculations were performed on the VAX 11/780 computer of the Theoretical Chemistry Group in Bologna.

Results

The 0–5 eV energy range ET spectra of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ and of its methyl and methoxy derivatives are reported in Figure 1. The spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^4\text{-}C_4H_6)Fe(CO)_3$, and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ are given in Figure 2.

All the spectra display a number of resonances much lower than the number of metal d and ligand π^* empty orbitals. This suggests that some resonances are likely due to the contribution of several

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Table I. Atomic Sphere Radii (au)

	r_M	$r_{C(O)}$	r_O	r_C	r_H	r_{out}
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	2.2244	1.6572	1.6879	1.7276	1.2878	7.3648
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	2.1730	1.6468	1.6812	1.7300	1.3000	7.2560
$(\eta^4\text{-}C_4H_6)Fe(CO)_3$	2.1206	1.6605	1.7031	1.7869	1.2870	7.2212
		1.6254	1.6617	1.7460	1.2429	
$(\eta^5\text{-}C_5H_5)Co(CO)_2$	2.1517	1.6806	1.7283	1.7640	1.3180	7.1519

Table II. Calculated and Experimental AEs and IEs of (Benzene)chromium Tricarbonyl[a]

AE								
exptl	Xα	C_{3v}	Cr	C_{ring}	$C_{(CO)}$	O	INT	OUT
3.63	3.2	a_2	0	39	13	6	25	17
2.4	1.9	a_2	1	20	27	12	35	5
1.82	1.8	e	9	1	12	7	20	51
	1.7	e	16	0	20	8	16	40
	1.2	a_1	12	1	15	6	15	52
0.96	1.0	e	34	3	8	4	20	31
	0.9	a_1	4	1	3	8	10	72
	0.1	e	18	6	3	6	43	24
	−0.1	e	13	48	4	2	30	3
EI								
7.42	7.3	a_1	69	1	3	11	16	0
	7.4	e	58	9	2	10	21	0
10.70	10.8	e	6	59	1	3	31	0

[a] The calculated transition-state charge distributions are also included. IE values taken from ref 13.

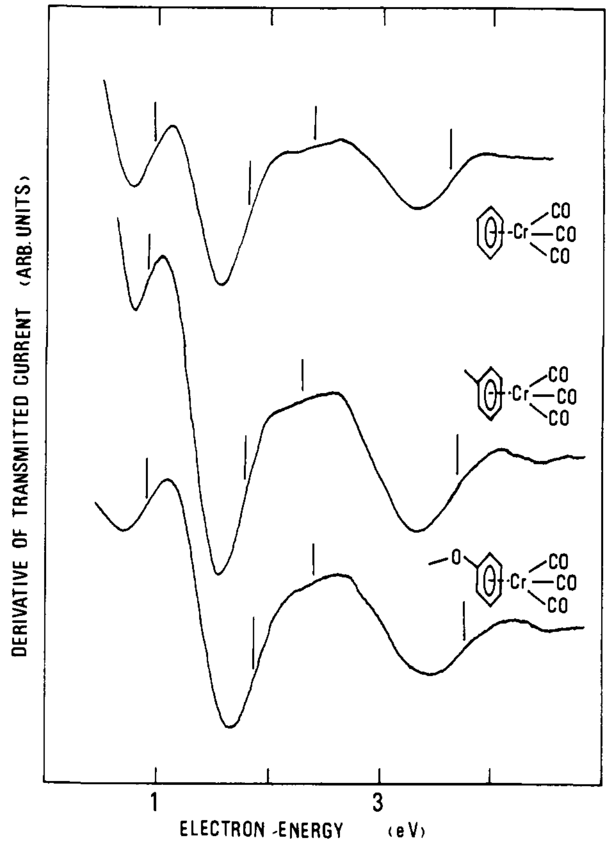

Figure 1. ET spectra of (arene)chromium tricarbonyls (arene = C_6H_6, $C_6H_5\text{–}CH_3$, $C_6H_6\text{–}OCH_3$).

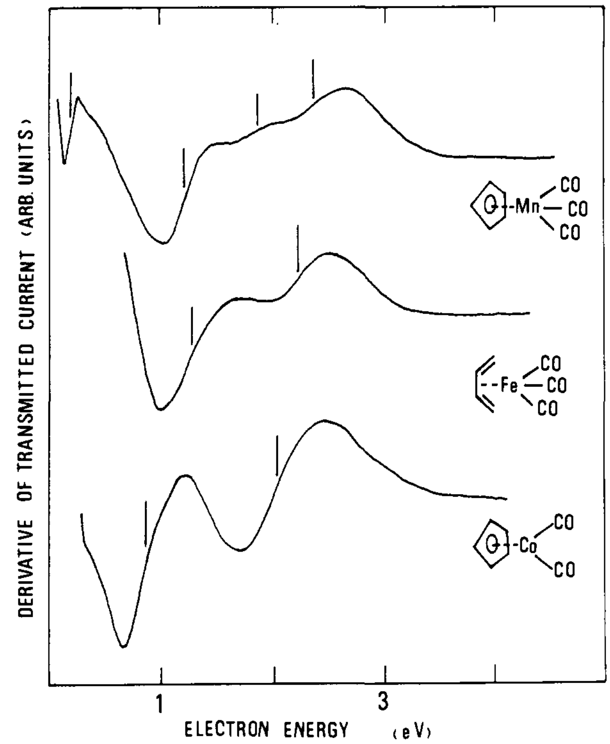

Figure 2. ET spectra of (cyclopentadienyl)manganese tricarbonyl, (1,3-butadiene)iron tricarbonyl, and (cyclopentadienyl)cobalt dicarbonyl.

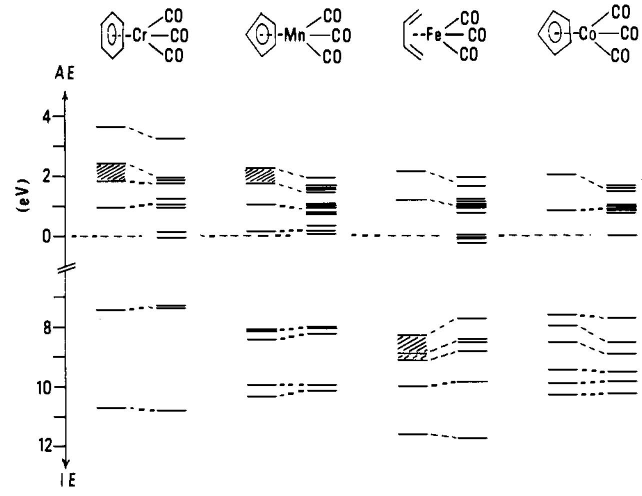

Figure 3. Correlation diagram of the experimental (ETS and UPS) and calculated (Xα) AEs and IEs. (IEs taken from ref 13, 14, 15 and 16.)

anion states unresolved in energy. Besides, some anion states could be stable (and thus inaccessible with ETS) or very close to zero energy (where they are masked by the intense transmitted electron beam signal).

The Xα results confirm these hypotheses and fully account for the observed spectral features, as shown in the correlation diagrams given in Figure 3. Moreover, the number of anion states calculated at low energy indicates that the anion states associated with electron capture into σ* metal–ligand orbitals also contribute to the observed spectra. Some of the calculated states with very large localization in the outersphere region, however, may not contribute significantly to the resonances observed experimentally.

The reliability of the theoretical method is tested by calculating the metal d and ligand π IEs. As shown in Figure 3, and in Tables II–V, the agreement with the experimental data is very good. In particular, the present calculations (see Table III) support the conclusion of Lichtenberger and Fenske[14] about the relative or-

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Table III. Calculated and Experimental AEs and IEs of (Cyclopentadienyl)manganese Tricarbonyl[a]

AE								
exptl	Xα	C_s	Mn	$C_{(cp)}$	$C_{(O)}$	O	INT	OUT
2.36	2.0	A″	3	1	24	8	18	46
	1.7	A″	4	2	15	9	20	50
1.8	1.6	A″	1	40	11	6	28	14
	1.6	A′	12	1	15	8	15	49
	1.5	A′	3	33	10	5	26	23
	1.1	A′	7	2	9	5	12	66
	1.0	A′	5	27	2	3	35	28
1.22	1.0	A″	6	24	3	4	32	31
	0.8	A″	26	5	6	3	27	33
	0.8	A′	24	6	6	2	25	37
	0.4	A′	7	2	4	10	43	34
0.2	0.2	A″	32	10	5	5	34	14
	0.1	A′	27	9	4	4	37	19
IE								
8.05	8.0	A″	64	7	2	10	27	0
	8.0	A′	64	7	2	10	27	0
8.40	8.2	A′	73	1	2	10	14	0
9.90	9.9	A′	15	53	1	3	30	0
10.29	10.1	A″	13	54	1	2	30	0

[a] The calculated transition-state charge distributions are also included. IE values taken from ref 14.

Table IV. Calculated and Experimental AEs and IEs of (1,3-Butadiene)iron Tricarbonyl[a]

AE								
exptl	Xα	C_s	Fe	$C_{(CC)}$	$C_{(CO)}$	O	INT	OUT
2.21	2.0	A″	2	2	19	11	17	59
	1.7	A″	2	35	20	8	28	6
	1.3	A′	6	0	18	9	16	47
	1.2	A″	6	13	6	2	15	59
1.26	1.1	A′	7	2	17	12	28	35
	1.0	A′	2	3	6	6	25	57
	1.0	A″	7	9	8	5	28	43
	0.8	A″	17	2	7	5	33	36
	0.1	A′	9	2	4	4	44	36
	0.0	A″	40	14	8	5	25	8
	0.0	A′	18	17	4	2	33	26
	−0.2	A′	12	16	5	3	42	22
IE								
8.23	7.7	A′	41	20	6	4	28	1
8.82	8.4	A′	64	6	2	9	19	0
	8.5	A″	56	13	2	9	20	0
9.09	8.8	A′	77	2	1	8	12	0
9.93	9.8	A″	27	43	1	3	26	0
11.52	11.7	A′	10	54	4	4	28	0

[a] The calculated transition-state charge distributions are also included. IE values taken from ref 15.

Table V. Calculated and Experimental AEs and IEs of (Cyclopentadienyl)cobalt Dicarbonyl[a]

AE								
exptl	Xα	C_s	Co	$C_{(cp)}$	$C_{(CO)}$	O	INT	OUT
	1.7	A″	1	38	8	4	23	26
2.05	1.6	A′	3	1	17	8	12	59
	1.5	A′	2	31	5	2	16	44
	1.0	A′	4	24	4	4	30	34
	1.0	A″	6	17	10	6	29	32
0.88	0.9	A″	7	5	14	7	24	43
	0.9	A′	7	2	14	6	13	58
	0.8	A′	7	3	11	12	35	32
	0.0	A′	48	14	10	5	19	4
IE								
7.59	7.7	A″	40	28	2	8	22	0
7.95	8.5	A′	78	3	2	4	13	0
8.51	8.9	A′	75	1	1	13	10	0
9.41	9.5	A″	80	2	1	9	8	0
9.87	9.8	A′	12	53	2	3	30	0
10.23	10.2	A″	41	37	0	3	19	0

[a] The calculated transition-state charge distributions are also included. IE values taken from ref 16.

Table VI. Calculated Charge Densities in the Neutral Ground States of (Benzene)chromium Tricarbonyl, (Cyclopentadienyl)manganese Tricarbonyl, (1,3-Butadiene)iron Tricarbonyl, and (Cyclopentadienyl)cobalt Dicarbonyl[a]

	charge (e)		
compound	metal	π ligand	carbonyls
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	−0.91 $(d^{5.69}s^{0.41}p^{0.68}f^{0.13})$	+1.16	−0.25
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	−0.81 $(d^{6.50}s^{0.43}p^{0.75}f^{0.13})$	+0.88	−0.07
$(\eta^4\text{-}C_4H_6)Fe(CO)_3$	−0.70 $(d^{7.29}s^{0.42}p^{0.87}f^{0.12})$	+0.60	+0.10
$(\eta^5\text{-}C_5H_5)Co(CO)_2$	−0.67 $(d^{8.16}s^{0.52}p^{0.86}f^{0.13})$	+0.68	−0.01

[a] The numbers in parentheses give the metal orbital populations above [Ar].

dering of the metal d(e) and d(a_1) (in the C_{3v} point group notation) IEs of the Mn complex. Also the large metal/ring mixing between the 7.6 and the 10.2 eV cation states of $(\eta^5\text{-}C_5H_5)Co(CO)_2$, predicted by Lichtenberger et al.[16] by comparing the He I and He II UPS spectra, is confirmed by the Xα calculations (see Table V).

Anion states which are stable or close to zero energy are calculated for all the complexes. Only the spectrum of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ shows an intense resonance at very low energy (0.2 eV). However, a shoulder on the high energy wing of the electron beam signal (not shown in the figures) was observed for the Cr and Fe complexes.

Discussion

The spectrum of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ displays four resonances below 5 eV. According to the calculations (see Table II), two ^2E anion states lie at −0.1 and 0.1 eV, with mainly ring π and metal d character, respectively. Following these, three anion states are calculated close in energy to the first resonance observed (0.96 eV). The first is expected to have a low cross section, its localization in the outer sphere being very high. The second and the third are significantly localized at the metal and at the carbonyl groups, respectively.

The next two resonances (1.82 and 2.4 eV— the 2.4-eV resonance has a larger relative intensity and is better resolved when the apparatus is operated in the low rejection mode) can be associated with the three anion states calculated at about 1.8 eV, two with mainly metal–carbonyl and one with mainly ring–carbonyl character.

Finally, the highest lying resonance in this energy region (3.63 eV) is expected to be correlated with electron capture into the benzene b_{2g} (π*) MO occurring at 4.82 eV[7] in the free ligand. In agreement, a $^2A_2$ anion state of largely ring character is calculated at 3.2 eV.

The large stabilization of this benzene resonance upon complex formation is somewhat surprising. In principle, a stabilization could arise from mixing with the empty 4s or 4p orbitals of chromium. This mechanism, however, is prevented for symmetry reasons. No contribution from the metal is, in fact, calculated for the A_2 anion state (see Table II). Another possible explanation lies in the ring C–C bond length increase on going from benzene (1.397 Å) to the complex (1.41 Å). This effect, however, has been calculated[6] to be small in bis(benzene)chromium, where the ring expansion is even larger.

The sizable stabilization of the highest lying benzene Π anion state upon complexation is accounted for by the charge distribution calculated in the neutral ground state (see Table VI), according to which the Cr atom has a large negative charge (−0.91 e) and

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the benzene ring a large positive charge (+1.16 e).

These results are in contrast with those obtained at the ab initio[13] and CNDO/2[17] levels. Several experimental data are, however, consistent with the strong ring-to-metal charge transfer, predicted by the present calculations. These are the following: (i) The first ionization energy (involving electron ejection from a metal d orbital) greatly decreases on going from $Cr(CO)_6$ (8.40 eV[18]) to (η^6-C_6H_6)$Cr(CO)_3$ (7.42 eV[13]) to (η^6-C_6H_6)$_2$Cr (5.45 eV[13]), that is, upon replacement of carbonyl by benzene ligands. Ionization from the core Cr 2p orbital displays the same energy trend, while the ring C 1s ionization energy increases on going from free benzene to the chromium complexes.[19] (ii) The acidity of benzoic acid is affected in the same direction by chromium complexation and by electron acceptor substituents on the ring.[20] (iii) Nucleophilic substitution of aromatic compounds is greatly favored upon complexation with Cr, Mn, and Fe tricarbonyls.[21,22] The electron-withdrawing effect of the $Cr(CO)_3$ group, for example, is estimated to be of the same order as that of a p-NO_2 group.[22]

Table II shows that both the $^2A_2$ anion states are characterized by sizable ring/carbonyl mixing, in spite of their very small localization at the central metal atom. This indicates the occurrence of direct through-space interaction between the cyclopentadienyl and the carbonyl groups. The same interaction was found to occur between the benzene ligands of bis(benzene)chromium.[6]

The ET spectra (see Figure 1) of (toluene)chromium tricarbonyl and (anisole)chromium tricarbonyl are very similar to that of the unsubstituted complex (AEs: 0.90, 1.80, 2.3 and 3.68 eV for the methyl derivative; 0.90, 1.80, 2.4, and 3.71 eV for the methoxy derivative). Previous ETS work[23] has shown the very small energy perturbation produced by the CH_3 substituent on the benzene Π anion states. In contrast, the oxygen lone pair/π^* charge-transfer interaction produces a sizable destabilization of the component of proper symmetry of the benzene $^2E_{2u}$ (Π) anion state.[24] The main effect of the OCH_3 substituent on (benzene)chromium tricarbonyl should thus be the destabilization of the component of proper symmetry of the ^2E anion state, the only one with large benzene $^2E_{2u}$ character (see Table II). The experimental finding that none of the observed resonances is shifted to higher energy on methoxy substitution is thus consistent with the theoretical prediction that the ^2E anion state of the chromium complex is stable.

In the Mn, Fe, and Co complexes the symmetry is lowered to C_s, allowing a large delocalization of the anion states over the whole molecule (see Tables III, IV, and V).

The lowest lying anion state in the Mn and Co cyclopentadienyl complexes is predicted to be of mainly metal character, anion states of prevalently cyclopentadienyl character being calculated at about 1.0 and 1.5 eV in both the complexes. In the iron complex, no anion state is predicted to possess a predominantly butadiene character, the contribution of the butadiene ligand being spread over several anion states.

The calculations predict a large negative charge at the metal atom and a large positive charge at the π ligand for the neutral states of the Mn, Fe, and Co complexes, as well as for the Cr complex, the carbonyl groups being almost neutral (see Table VI).

On the basis of these results, the ligand field nomenclature d^6 and d^8 respectively for Mn and Co, which implies a metal-to-ligand electron transfer, is misleading. On the contrary, all the metal atoms show a strong overall negative charge increase upon complexation. According to the calculations, the 4s and 4p orbitals play an important role in this net π-ligand → metal charge transfer, the electronic charge gained by these orbitals being much larger than that lost by the 3d orbitals.

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Registry No. (η^6-C_6H_6)$Cr(CO)_3$, 12082-08-5; (η^5-C_5H_5)$Mn(CO)_3$, 12079-65-1; (η^4-C_4H_6)$Fe(CO)_3$, 12078-32-9; (η^5-C_5H_5)$Co(CO)_2$, 12078-25-0; (η^6-$CH_3C_6H_5$)$Cr(CO)_3$, 12083-24-8; (η^6-$CH_3OC_6H_5$)$Cr(CO)_3$, 12116-44-8.

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