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Negative Ion States of 3d Metallocenes

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Abstract: The energies of the low-lying, unstable negative ion states of the 3d metallocenes $M(Cp)_2$ (M = V, Cr, Mn, Fe, Co, Ni) have been obtained by electron transmission spectroscopy. For the last three members of the series (M = Fe, Co, Ni) calculations employing the multiple scattering $X\alpha$ method with stabilization permit the assignment of the observed states to electron capture into the metal 3d, $4e_{1g}$ orbital or cyclopentadienyl π^* orbitals.

Over the past decade the ionization potentials of a great variety of gas-phase organometallic molecules have been studied by photoelectron spectroscopy (PES) in order to characterize the occupied valence orbitals. The unoccupied (virtual) orbitals have been neglected. There have been published only three electron-scattering studies which provide information on the electron affinities of organometallic molecules in the gas phase.[1-3] This is unfortunate since information on the unoccupied orbitals is needed to complete the picture of the electronic structure of these molecules and to understand the nature of charge-transfer reactions wherein these orbitals come into play.[4] Electron affinities can be obtained by electron transmission spectroscopy[5-7] (ETS), the experiment conjugate to PES. Whereas PES measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of a negative ion state arising from electron capture into an unoccupied orbital. In this paper we present the results of an ETS study of the first transition series metallocenes.

The bis(π-cyclopentadienyl) compounds of the first transition series are isomorphous.[8,9] With the exception of manganocene, the chemical and physical properties of these metallocenes are remarkedly similar. The rings are covalently bonded to the metal atom except in the case of manganocene which is believed to be ionically bonded. This is reflected in the greater ring-to-metal distance in manganocene compared to the other metallocenes and by its chemical and physical properties.

The electronic configurations and electronic states of the first transition series metallocenes $M(Cp)_2$ (M = V, Cr, Mn, Fe, Co, Ni) are given in Table I. The $3e_{2g}$ and $5a_{1g}$ orbitals are essentially metal d orbitals. the $4e_{1g}$ is antibonding with metal $d\pi$ and ligand π contributions. $V(Cp)_2$ and $Cr(Cp)_2$ are high spin complexes since the $3e_{2g}$ and $5a_{1g}$ orbitals have nearly the same energy. $Mn(Cp)_2$ may be either high or low spin, but the high-spin complex is believed to predominate in the gas phase.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector.[10] In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.[11] The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which characterize the resonance. For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity (EA).[12] The chief limitation is that ETS gives only the energy associated with unstable negative ions. That is, only negative electron affinities can be obtained with ETS.

Table I. Orbital Occupations and Ground Electronic States of Metallocenes

$V(Cp)_2$	$(3e_{2g})^2(5a_{1g})^1$	$^4A_{2g}$
$Cr(Cp)_2$	$(3e_{2g})^3(5a_{1g})^1$	$^3E_{2g}$
$Mn(Cp)_2$	$(3e_{2g})^4(5a_{1g})^1$	$^2A_{1g}$ or $(3e_{2g})^2(5a_{1g})^1(4e_{1g})^2$ $^6A_{1g}$
$Fe(Cp)_2$	$(3e_{2g})^4(5a_{1g})^2$	$^1A_{1g}$
$Co(Cp)_2$	$(3e_{2g})^4(5a_{1g})^2(4e_{1g})^1$	$^2E_{1g}$
$Ni(Cp)_2$	$(3e_{2g})^4(5a_{1g})^2(4e_{1g})^2$	$^3A_{2g}$

Table II. Calculated and Experimental lonization Potentials (eV) of $3e_{2g}$ and $5a_{1g}$ Electronics in $Fe(Cp)_2$

ion state	exptl[a]	MS-Xα[b]	MS-Xα[c]	DVM Xα[d]	Hartree-Fock[e]
$^2E_{2g}$	6.9	8.5	7.7	6.7	5.7
$^2A_{1g}$	7.2	7.9	7.3	6.7	7.5

[a] Reference 27. [b] Reference 18. [c] Present work. [d] Reference 21. [e] Reference 24.

The samples were obtained from commercial sources. Because certain of them are sensitive to air, moisture, and light, the samples were handled in a glovebox under dry nitrogen and subdued light. Except for manganocene the samples were heated to 45 °C in order to obtain a sufficient vapor pressure. Manganocene required a temperature of 80 °C and vapor from this compound caused the spectrometer to behave erratically. There was also some evidence of decomposition or reaction of this sample. Clearly the manganocene data must be regarded with suspicion.

Results

The derivative spectra are presented in Figure 1. They are similar in that each spectrum has a feature between 0 and 1 eV and a feature near 2.5 eV. For $Mn(Cp)_2$ and $Ni(Cp)_2$ the low-energy resonance is so close to 0 eV that it appears only as a broadening of the spike which represents the derivative of the sharp

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(1) Giordan, J. C.; Moore, J. H.; Tossell, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 6632.

(2) Begun, G. M.; Compton, R. N. *J. Chem. Phys.* **1973**, *58*, 2271.

(3) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 47.

(4) Holloway, J. D. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2038, and references therein.

(5) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 344.

(6) Schulz, G. J. *Rev. Mod. Phys.* **1973**, *45*, 379.

(7) Schulz, G. J. *Rev. Mod. Phys.* **1973**, *45*, 423.

(8) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; pp 542-54.

(9) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; pp 777-8.

(10) Stamatovic, Al; Schulz, G. J. *Rev. Sci. Instrum.* **1970**, *41*, 423. McMillan, M. R.; Moore, J. H. *Ibid.* **1980**, *51*, 944.

(11) Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *45*, 1672.

(12) For a discussion of AE's vs. EA's as well as calibration of the ETS spectrum see: Giordan, J. C.; McMillan, M. R.; Moore, J. H.; Staley, S. W. *J. Am. Chem. Soc.* **1980**, 102, 4870.

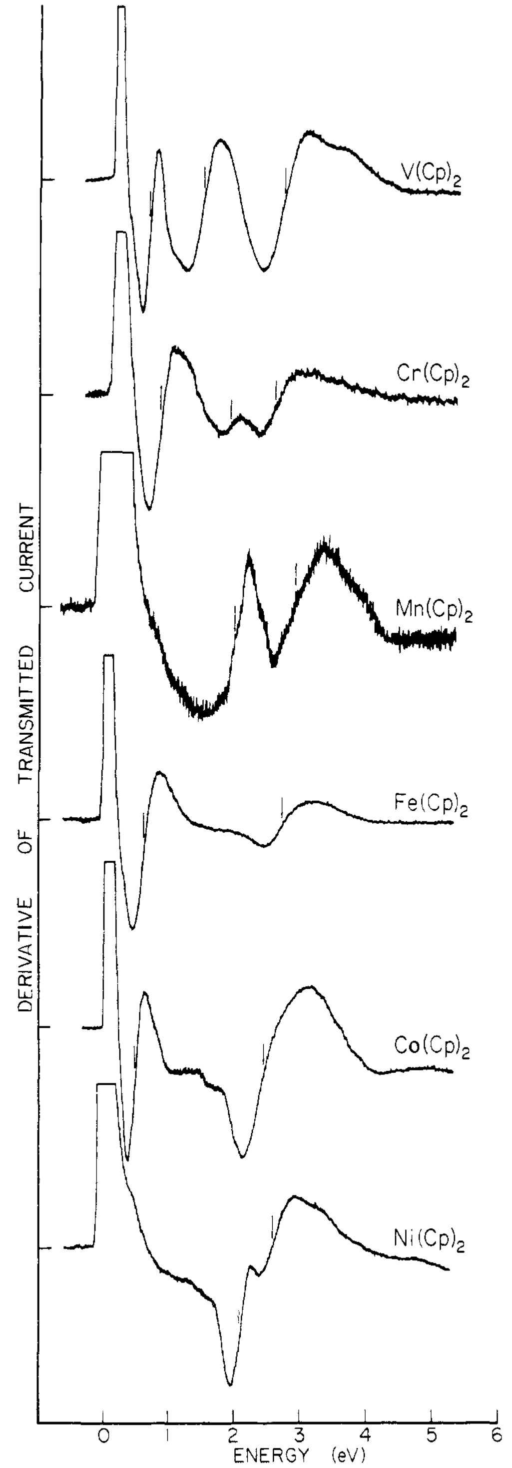

Figure 1. Derivative electron transmission spectra of the 3d metallocenes, $M(Cp)_2$ (M = V, Cr, Mn, Fe, Co, Ni). Each spectrum was calibrated against that of nitrogen (see refer 12).

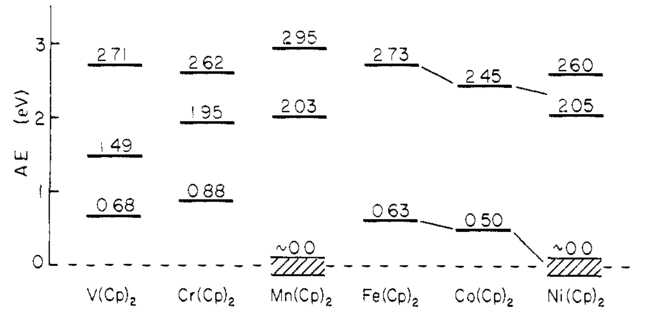

Figure 2. Correlation diagram giving attachment energies of the 3d metallocenes. The uncertainty in the measurements is ±0.1 eV.

rise of current at 0 eV. For the first three members of the series a feature appears between 1.5 and 2.0 eV. For ease of discussion the attachment energies obtained from the spectra are arranged in a correlation diagram in Figure 2.

Discussion

To properly describe temporary negative ion formation, a formal scattering calculation is required. Accurate scattering solutions have been obtained for small molecules,[13] but most studies of electron scattering by large molecules have employed the multiple scattering Xα (MS-Xα) method.[14] Notable examples to this approach are studies of SF_6[15] and substituted hydrocarbons.[16] The bound-state version of the MS-Xα method[17] has successfully predicted many of the properties of $Fe(Cp)_2$,[18] $Co(Cp)_2$,[19] and $Ni(Cp)_2$.[20] $Fe(Cp)_2$ and $Co(Cp)_2$ have also been studied by the Xα discrete variation method,[21,22] and $Fe(Cp)_2$ has been the subject of ab initio self-consistent field studies.[23,24] The first three members of the metallocene series have so far been studied only by approximate SCF methods.[25,26] In Table II we compare ionization potentials calculated by various methods for the predominantly Fe 3d orbitals of $Fe(Cp)_2$. It is apparent from these examples that all methods give errors in the range of a few tenths of an electronvolt to slightly more than 1 eV. Certainly no higher accuracy can be expected in the calculation of attachment energies.

In our work on the d^6 metal hexacarbonyls[1] we found that the transition state method[28] applied to a bound-state Xα calculation could be used to give a plausible interpretation of the electron transmission spectra. To obtain ionization potentials with this method, one calculates eigenvalues for a transition-state electronic configuration wherein half an electron is removed from the orbital from which ionization occurs. Similarly the electron affinity is obtained from the calculation of the eigenvalue for the transition state in which half an electron is added to the orbital which is occupied in creating the anion. In the previous calculations the molecule was immersed in a sphere of charge (a Watson sphere)[29] with sufficient potential to give negative eigenvalues in the transition state. The energy of stabilization of the Watson sphere was added to the eigenvalue to give the electron affinity. This scheme is essentially a simplified stabilization method.[30] For localized empty orbitals in simple systems, maxima in electron-scattering cross sections obtained using the formalism of Dill and Dehmer[14] are probably close in energy to empty orbital eigenvalues. For example, in CO the π channel scattering maximum is within 0.1 eV of the π* orbital eigenvalue (Tossell, unpublished calculations). However, such a simple interpretation may not be possible if a number of different symmetry channels give significant contributions to the cross section or if the molecule has a large electric dipole polarizability which strongly stabilizes the anion.

In the following we apply our stabilized Xα analysis to $Fe(Cp)_2$,

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(13) Klonover, A.; Kaldor, U. *J. Phys. B.* **1978**, *11*, 1623.

(14) Dill, D.; Dehmer, J. L. *J. Chem. Phys.* **1974**, *61*, 692.

(15) Dehmer, J. L.; Siegel, J.; Dill, D. *J. Chem. Phys.* **1978**, *69*, 5205.

(16) Bloor, J. E.; Sherrod, R. E.; Grim, F. A. *Chem. Phys. Lett.* **1981**, *78*, 351.

(17) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.

(18) Rösch, N.; Johnson, K. H. *Chem. Phys. Lett.* **1974**, *24*, 179.

(19) Weber, J.; Goursot, A.; Pênigault, E.; Ammeter, J. H.; Bachmann, J. *J. Am. Chem. Soc.* **1982**, *104*, 1491.

(20) Goursot, A.; Pênigault, E.; Weber, J. *Nouv. J. Chim.* **1979**, *3*, 675.

(21) Baerends, E. J.; Ros, P. *Chem. Phys. Lett.* **1973**, *23*, 391.

(22) Famiglietti, C.; Baerends, E. *J. Chem. Phys.* **1981**, *62*, 407.

(23) Rohmer, M. M; Veillard, A. *Chem. Phys.* **1975**, *11*, 349.

(24) Bagus, P. S.; Walgren, U. I.; Almlof, J. *J. Chem. Phys.*, **1976**, *64*, 2324.

(25) Armstrong, D. R., Fortune, R.; Perkins, P. G. *J. Organomet. Chem.* **1976**, *111*, 197.

(26) Clack, D. W.; Warren, K. D. *Inorg. Chim. Acta* **1978**, *30*, 251.

(27) Rabalais, J. W.; Werme, L. O.; Bergmark, T.; Karlsson, L.; Hussian, M.; Siegbahn, K. *J. Chem. Phys.* **1972**, *57*, 1185.

(28) Slater, J. C. "Quantum Theory of Molecules and Solids"; McGraw-Hill: New York, 1974; Vol. 4.

(29) Watson, R. E. *Phys. Rev.* **1953**, *111*, 1108.

(30) Taylor, H. S. *Adv. Chem. Phys.* **1970**, *18*, 91.

Table III. Calculated Attachment Energies (eV) for Occupation of $4e_{1g}$, $4e_{2g}$, and $3e_{2u}$ Orbitals in $Fe(Cp)_2$, $Co(Cp)_2$ (Spin-Polarized Case), and $Ni(Cp)_2$

	$Fe(Cp)_2$	$Co(Cp)_2$	$Ni(Cp)_2$
$4e_{1g}$	1.15	0.93[a], −0.47[b]	−0.13
$4e_{2g}$	1.19	1.16	1.14
$3e_{2u}$	3.26	3.49	3.68

[a] Average AE for singlet states ($^1A_{1g}$ + $^1E_{2g}$). [b] AE for $^3A_{2g}$ state.

$Co(Cp)_2$, and $Ni(Cp)_2$. For $Co(Cp)_2$ without spin polarization the calculated $4e_{1g}$ eigenvalue in the transition state with 0.5 electron in the $4e_{1g}$, corrected for the potential of the Watson sphere, is 0.54 eV. The parameters used in the calculation are identical with those used in previous work except that a Watson sphere with charge +2.0 and radius twice that of the outer sphere was imposed. Similar calculations (without spin polarization) yield the values (Table III) of 1.15 and −0.13 eV for the $4e_{1g}$ eigenvalues in $Fe(Cp)_2$ and $Ni(Cp)_2$, respectively. Parameters for the $Fe(Cp)_2$ calculation were chosen in the same way as for Co and Ni metallocenes with an Fe–ring distance of 1.65 Å[31] (shorter than that of 1.72 Å employed in a previous Xα calculation). These results are in reasonable agreement with the experimental data, showing the proper trend across the series and yielding a stable negative ion for the case of $Ni(Cp)_2$. Qualitatively, the $4e_{1g}$ attachment energy is expected to decrease across the series $Fe(Cp)_2$, $Co(Cp)_2$, $Ni(Cp)_2$, both because of a lowering of average 3d orbital energy with increasing atomic number and because of a decrease in the destabilization of the antibonding $4e_{1g}$ orbital as the metal–ring distance increases across the series.

It is worth noting that the $4e_{1g}$ AE may also be estimated by adding together the $4e_{1g}$ eigenvalue for a ground-state molecule without a Watson sphere and the magnitude of the change which occurs in that eigenvalue when the orbital occupation is reduced by 0.5 electron as in going to the photoionization transition state. The result obtained for $Co(Cp)_2$ is 0.49 eV, essentially identical with that from the previous approach. Employing this approach and using spin polarized eigenvalues for the ground state of $Co(Cp)_2$, we obtain attachment energies of 0.93 eV for the average AE of the singlet negative ion states ($^1A_{1g}$ + $^1E_{2g}$) and −0.47 eV for the $^3A_{2g}$ state. The presence of the stable negative ion for $Co(Cp)_2$ (not observable in our ETS experiment) is consistent with the results of Begun and Compton.[2] For the previous MS-Xα calculation[18] on $Fe(Cp)_2$ this approach yields an AE of 0.4 eV (with the lower value resulting at least partly from the longer Fe–ring distance) and the DVM-Xα calculation[21] on $Co(Cp)_2$ gives an AE of 0.7 eV. Thus although the precise value calculated varies somewhat with calculational scheme and the choice of parameters, all the Xα calculations give values in reasonable agreement with experiment. Hartree–Fock calculations,[23] on the other hand, predict a stable negative ion for $Fe(Cp)_2$, inconsistent with both our results and those of Begun and Compton. Since the AE values are all quite small, it is also plausible that our bound-state approximation should introduce no great error. Indeed, both the unstable and stable anions arising from addition of an electron to the $4e_{1g}$ orbital seem to be accurately described by this scheme with the absolute errors in their calculated energy being no greater than those found in the calculation of occupied M3d orbital ionization potentials.

We cannot presently offer so convincing an interpretation of the low-energy features in $V(Cp)_2$, $Cr(Cp)_2$, and $Mn(Cp)_2$. The principal difficulty lies in the large spin multiplicity of these species, which is expected to cause a large splitting of spin-up and spin-down M 3d levels. MS-Xα calculations are presently in progress.

Our interpretation of the high-energy ETS features for the metallocenes also remains somewhat speculative. Calculations on the ground state of neutral $Co(Cp)_2$ stabilized by the Watson sphere yield a number of orbitals with negative eigenvalues, most of which are quite diffuse or Rydberg-like. The orbitals corresponding to the cyclopentadienyl π* orbitals are the $4e_{2g}$ and the $3e_{2u}$. Attachment energies calculated for these orbitals (from transition-state eigenvalues corrected for the Watson sphere potential) are listed in Table III. The low AE calculated for the $4e_{2g}$ orbital is partly due to its small transition-state destabilization (1.3 eV vs. 2.5 eV for $3e_{2u}$ and 2.7 eV for $4e_{1g}$) and is a consequence of its diffuse nature (33% of the electron density in the outer sphere region compared to zero for the $3e_{2u}$). We anticipate that the scattering intensity from this orbital (and others with even greater Rydberg character) will be low, although this must be checked by later scattering calculations. Thus the $3e_{2u}$ orbital is probably mainly responsible for the ETS peak between 2.4 and 3.0 eV. Our calculated values may be higher than experiment because of the muffin-tin form of the potential (which underestimates the stability of the Cp π-type orbitals by about half an electronvolt even with an empty sphere at the ring center) and our neglect of the polarization of the $M(Cp)_2$ species by the approaching electron which would also lower the resonance energy. Since the wavelength of a 2–3-eV electron is of the same order as the size of the molecule, it may be that our neglect of nonspherical components in the outer-sphere potential introduces substantial error. We have implicitly assumed that the electron interacts with the whole molecule rather than a part of it, e.g., a single Cp^- ring. Further computations would be necessary to address this point.

Table IV. Comparison of Results (eV) of Begun and Compton (BC) with Present Results (GMTW)

	$Fe(Cp)_2$		$Co(Cp)_2$		$Ni(Cp)_2$	
	GMTW	BC	GMTW	BC	GMTW	BC
M 3d	0.63	0.5	0.50	~0.0, 0.5	~0.0	~0.0
Cp π*	2.73		2.45	2.4	2.05, 2.60	

The only other data on temporary negative ion states of the metallocenes are those obtained by Begun and Compton[2] in low-energy, low-resolution electron-scattering experiments on $Fe(Cp)_2$, $Co(Cp)_2$, and $Ni(Cp)_2$. As shown in Table IV their observations agree with the present data in every case but one.[32] In $Co(Cp)_2$ we observe the $4e_{1g}$ resonance at 0.50 eV, whereas Begun and Compton observe temporary negative ion states at 0.5 and ~0.0 eV corresponding to our $^3A_{2g}$ and $^1A_{2g}$ states. As noted before, the triplet state is marginally stable and thus does not appear in the electron transmission spectrum and the 0.50-eV resonance corresponds to the singlet state. It is noteworthy that the temporary negative ions observed by Begun and Compton have lifetimes of many microseconds, whereas the broad structureless resonances in the electron transmission spectra imply lifetimes of 10^{-12} s or less.[5] Apparently there are at least two modes of decay for the temporary negative ion. Perhaps some of the ions achieve stability by geometric rearrangement. Qualitative MO studies by Lauher and Hoffman[33] indicate that the $4e_{1g}$ orbital may be stabilized as much as 1 eV by bending of the structure to give a ring center–M–ring center angle less than 180°. In the work of Begun and Compton (Figures 7 and 8)[2] a maximum in $Co(Cp)_2^-$ production occurs at about 0 eV, a maximum in $Co(Cp)^-$ production occurs at 0.6 eV, and a maximum in Cp^- formation occurs at about 2.0 eV. The first two processes correspond to addition of an electron to the $4e_{1g}$ (M 3d) orbital while the process near 2.0 eV corresponds to adding an electron to a Cp π* orbital.

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Registry No. $V(Cp)_2$, 1277-47-0; $Cr(Cp)_2$, 1271-24-5; $Mn(Cp)_2$, 73138-26-8; $Fe(Cp)_2$, 102-54-5; $Co(Cp)_2$, 1277-43-6; $Ni(Cp)_2$, 1271-28-9.

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(31) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1068.

(32) In addition to the resonances noted, Begun and Compton report a resonance in $Ni(Cp)_2$ at about 1.1 eV. We observed a resonance at 1.14 eV only after the sample had been exposed to air.

(33) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.