

unit reactions minimally needed to convert one to another.

The intent of the SYNGEN program is then to provide an optimal set of synthetic sequences to a target from real starting materials, and this set can then be used as a basis of comparison with routes otherwise created by the imaginations of practicing chemists. A specific analytical tool is provided, in the total weight of required starting materials, to make such a comparison. This is not to say that the sequential construction

routes found here are necessarily the best; a truly elegant synthesis can still be shorter, but a basis for comparison is at least provided. In any case, our goal is not to replace "art in organic synthesis", but to provide standards of comparison against which true art will be more clearly seen.

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Anion States of Organometallic Molecules and Their Ligands

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Central to the understanding of the structure and reactivity of organometallic compounds is the need to characterize the properties of the ligand-to-metal bond. Heterogeneous catalysis at metal surfaces, homogeneous catalysis, the biological activity associated with metal centers (e.g., nitrogen fixation and the transport of O₂ in the blood), the ability of metal complexes to undergo substitution and isomerization reactions, and the ability to influence the regioselectivity of nucleophilic addition to unsaturated ligands are all governed by the reactivity and lability of specific ligand-to-metal bonds.

These bonds are intriguing in that they are basically coordinate covalent with the ligand supplying both of the required electrons. A theory describing complex formation between an electropositive metal and electron-donating ligands must account for the electron density distribution as well as the spatial orientation of the ligands. Pauling suggested back-bonding as a mechanism for delocalization of electron density on the metal.¹

In back-bonding, electron density from the metal is transferred onto the ligand, thus reinforcing the bond between the two centers and reducing the magnitude of charge separation. When incorporating this idea into molecular orbital theory, one distinguishes two types of ligand orbitals, those of σ -symmetry and those of

π -symmetry with respect to the metal-ligand bond axis. A metal-ligand σ complex forms as a result of overlap between ligand and metal atomic orbitals; this overlap is however modified by interaction of the metal-complex orbitals with filled or unfilled orbitals of π -symmetry on the ligand.² This is illustrated in Figure 1 for the case of a typical octahedral complex. The metal d orbitals are split in the field of the ligands to give the differentiated σ -complex orbitals t_{2g} and e_g .

For many important ligands there is also the possibility of a π interaction with the σ -complex. This would be the case for CO, which has π^* orbitals of appropriate symmetry, or for ligands such as PR₃ where orbitals on the ligating atom also have π symmetry with respect to the metal-ligand bond axis. This interaction results in a stabilization of the occupied bonding orbitals of the complex (t_{2g}) at no cost in energy since the t_{2g}^* orbitals which are concurrently destabilized are unoccupied. Thus, there is a redistribution of charge, or a back-bonding, away from the electropositive metal center onto unoccupied orbitals of the ligand with a concomitant increase in bond energy.

This back-bonding may give rise in some cases to only subtle energy differences in the molecule while in others, as in the case of some metal carbonyls, larger energy changes can occur resulting in complexes for which the first optical transition is so high in energy as to render the complex colorless. In addition, the extent of back-bonding between the metal and certain ligands governs ligand lability in competitive substitution reactions.

To appreciate back-bonding fully requires a knowledge of both the energy and orbital character of the participating unoccupied ligand orbital. Electron transmission spectroscopy (ETS) is an experimental technique which can aid in this.³ This method measures gas-phase electron affinities corresponding to

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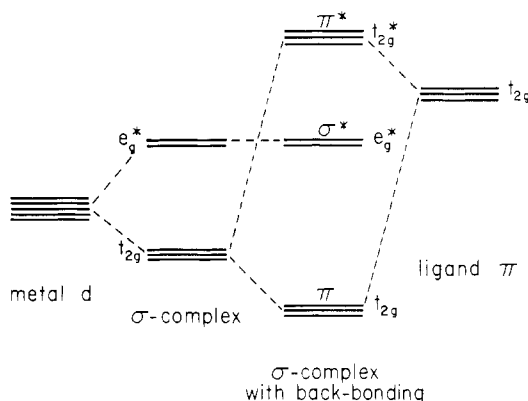


Figure 1. Metal-ligand orbitals can be of either σ or π symmetry with respect to the metal-ligand bond axis. This diagram illustrates the effect of π -type interactions of an acceptor ligand orbital with the metal-ligand complex arising from σ -type interactions in an octahedral complex. The effect is to stabilize occupied orbitals at the expense of unoccupied orbitals.

electron capture into low-lying unoccupied molecular orbitals. For present purposes such a measurement is superior to observation of an optical transition, where the energy of the final state is influenced by the hole left by the electron which is promoted to the orbital of interest. With ETS a correlation can be sought between the energies of anion states and properties of ligands of known π -acceptor characteristics.

Research directed towards understanding the properties of unfilled ligand orbitals and π -type interactions with these orbitals has proceeded along three paths: (i) The energies of anion states of ligands or models for ligands have been measured by ETS; (ii) π interactions with ligands have been assessed through studies of perturbations of state energies in benzenoid systems with model ligands as substituents; (iii) The energies of anion states of highly symmetrical transition metal complexes have been measured.

Electron transmission spectroscopy (ETS) is the conjugate to photoelectron spectroscopy (PES). Whereas PES measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of the anion state arising from electron capture into an unoccupied orbital. Data from both experiments can often be interpreted in a Koopmans' theorem⁴ sense to elucidate a change in the energy of a particular orbital through an homologous series of molecules.

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 kinetic 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. In practice the first

(4) Koopmans' theorem identifies the ionization potential of an electron in a particular orbital with the eigenvalue of the orbital. An independent-particle representation of molecular electrons is assumed.

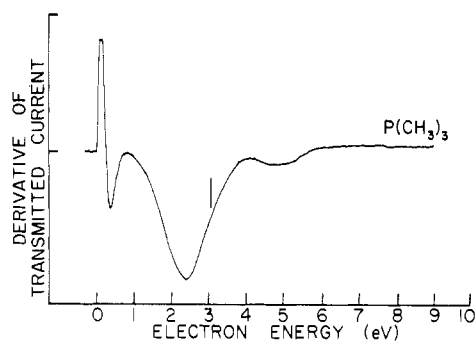


Figure 2. Derivative electron transmission spectrum of trimethylphosphine. A tick mark indicates the position of the electron scattering resonance due to electron capture into the lowest energy unoccupied σ^* orbital. Features near 0 eV are explained in the text.

derivative of the transmitted current as a function of electron energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.⁵ 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 that characterize the resonance. For the present purposes an attachment energy can be identified with the negative of the corresponding electron affinity.

A typical electron transmission spectrum is shown in Figure 2, as well as in other figures throughout this Account. Two low-energy features are apparent in most electron transmission spectra. These are (1) a "turn-on" spike which is simply the derivative of the step associated with the abrupt turn-on of current near 0 eV, and (2) a "retarding cusp" which is the relatively sharp minimum following on the heels of the first feature. The turn-on feature is sharp if the instrument is properly adjusted to provide maximum current from near 0 eV upwards, and if the band-pass of the electron monochromator is narrow. The turn-on feature is characteristically broadened if the target possesses an anion state whose energy is slightly below or slightly above 0 eV. The cusp is a well-known instrumental artifact whose position depends upon the tuning of the instrument.⁶

Ligands

The π -acceptor strength of ligands has been assessed from analysis of metal-to-ligand bond distances,⁷ vibrational frequencies,^{8,9} electron-binding energies,¹⁰ and from ease of displacement in ligand-substitution reactions.¹¹ A quantitative assessment of force constants using the Cotton-Kraihanzel force-field technique has established a π -acceptor series:⁸ $\text{NO} > \text{CO} \sim \text{RNC} \sim$

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Table I.
Attachment Energies (AE) to the Lowest Unoccupied
Orbital of Main Group Hydrides and Methides:
Attachment Energy to CO is Included for Comparison

hydride	AE, eV	methide	AE, eV
group 14			
CH ₄	8 ^a	C(CH ₃) ₄	6.1 ^e
SiH ₄	2.0 ^{b,c}	Si(CH ₃) ₄	3.9 ^e
		Ge(CH ₃) ₄	3.7 ^e
		Sn(CH ₃) ₄	2.9 ^e
group 15			
PH ₃	1.9 ^c	N(CH ₃) ₃	4.8 ^f
		P(CH ₃) ₃	3.1 ^f
		As(CH ₃) ₃	2.7 ^f
group 16			
H ₂ S	2.1 ^{c,d}	(CH ₃) ₂ O	6.0 ^f
		(CH ₃) ₂ S	3.3 ^f
group 17			
HCl	3.3 ^c	CH ₃ F	6.2 ^g
		CH ₃ Cl	3.7 ^{g,h}
		CH ₃ Br	~0 ^g
		CH ₃ I	<0 ^g
CO	2.0 ⁱ		

^a Reference 12. ^b Reference 13. ^c Reference 14. ^d Reference 5b.
^e Reference 15. ^f Reference 16. ^g Reference 17. ^h Reference 18.
ⁱ Reference 3.

PF₃ > PCl₃ > PCl₂OR > PCl₂R > PBr₂R > PCl(PClR₂) > P(OR)₃ > PR₃ ~ SR₂ > RCN > *o*-phenanthroline > alkyl amines, esters, ethers. In general, ligands are good π -acceptors if they possess a symmetry-correct unoccupied orbital with an energy similar to that of the π -acceptor orbital in CO, and if the ligand is relatively electronegative. To provide a systematic understanding of the energies of these unoccupied orbitals, a large number of simple group 14–17 compounds, MR_m (R = H, CH₃), have been studied by electron transmission spectroscopy. Many of these compounds commonly function as ligands in coordination chemistry or may serve as models of common ligands.

The electron transmission spectra of these compounds are quite simple, consisting usually of a single broad resonance as illustrated for P(CH₃)₃ in Figure 2. Resonance energies for main-group hydrides and methides are collected in Table I.

For these compounds the electron scattering resonance is associated with electron capture into low-energy valence-type molecular orbitals (for example, the 2t₂ in SiH₄, the 3e in PH₃, the 3b₂ in H₂S). These are antibonding orbitals characterized by a node between the central atom and each H or methyl group. These orbitals are probably best described as σ^* molecular orbitals rather than atomic d functions on the central atom. This distinction is made on the basis of orbital composition and extent (see for example the calculations and contour plots in ref 19 (SiH₄), 20 (PH₃), and 21 (H₂S)) and says nothing about orbital symmetry which may be such as to allow d-orbital participation.¹⁴

It is noteworthy that the resonance energy increases when methyl groups replace hydrogens in any of these compounds.^{13,14} The π -acceptor series similarly reflects

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Table II.
Correlation of properties of Cr(CO)₅L with Attachment
Energies of the Ligand L

L	AE (eV) of L	"t _{2g} " splitting, eV ^a	" π acceptance" of L, mdyn/Å ^b
CO	2.0 ^c	0	0.74
N(CH ₃) ₃	4.8	0.31	0.0
PH ₃	1.9	0.13	
P(CH ₃) ₃	3.1	0.14	0.48
S(CH ₃) ₂	3.3	0.20	0.15

^a Reference 22. ^b Reference 23. ^c Reference 3.

a chemical sensitivity to substitution on the central atom of a ligand. The implied sensitivity of orbital energy to substitution corroborates the contention that the orbitals involved are of such an extent that they are best described as molecular orbitals.

As the data suggest, for all compounds of first row elements, the empty σ^* orbital is relatively high in energy compared to the π^* orbital in CO. This accounts in part for the unavailability of this orbital for π -back-bonding, and hence the location of these ligands in the π -acceptor-strength series. On descending the periodic table the σ^* orbital is stabilized, and the ability of the ligand to back-bond increases substantially.

Analysis of the properties of substituted carbonyls such as Cr(CO)₅L, where L is a two-electron-donor ligand such as PH₃, shows a correlation between ligand AE and chromium 3d-L π -bonding effects. Representative data are given in Table II. When L is a strong π acceptor such as P(CH₃)₃, the effective symmetry at the Cr atom is nearly octahedral and the occupied metal 3d orbital (of t_{2g} symmetry in octahedral symmetry) is almost unsplit.²² When L is a poor π -acceptor such as N(CH₃)₃, the splitting of this orbital is substantial. Trends in the AE's of other ligands L are qualitatively consistent with their observed effects on chromium 3d orbital binding energies; thus, for example, (CH₃)₂S has a moderately high AE, a moderate π -acceptor ability and gives an intermediate "t_{2g}" orbital splitting. IR and Raman spectra may also be used to generate scales of σ -donor and π -acceptor strength for ligands.²³ CO is found to have the strongest π -acceptor character and nitrogen bases the weakest. Again, a general correlation is observed between the AE of the ligand and its π -acceptor character.

Interaction Model Compounds

The effect of substitution of benzene has for years provided a basis for models describing substituent effects upon ultraviolet spectra, photoelectron spectra, and chemical reactivity of organic systems. These models make use of a molecular orbital picture and describe substituent effects by focusing on the perturbations to the outermost occupied and innermost unoccupied orbitals of benzene as a result of interaction with the orbitals on the substituent. Usually perturbations of benzene are separated into resonance and inductive contributions resulting from separate π and σ interactions with the substituent.²⁴ Para-disubsti-

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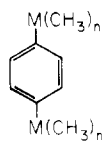
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tuted benzenes have been studied extensively. Al-



though σ -type interactions between a substituent and the benzene system differ from the interactions between ligands and metals, we believe that the perturbation of benzene π and π^* orbitals caused by substituent-based molecular orbitals reflect the nature of π -type interactions of ligand orbitals with atomic orbitals on a metal center. The range of substituents chosen reflects the range of monodentate ligand-metal interactions that can be anticipated. The group 14 compounds are not very electronegative; the ligand-based molecular orbitals do however extend above and below the plane of the benzene affording the possibility of a pseudo- π interaction which mimics the d_{π} - p_{π} interaction in organometallic compounds such as $\text{Cr}(\text{CO})_6$. At the opposite extreme, the group 17 substituents are very electronegative and can be expected to experience an inductive interaction. The observation of orbital perturbations associated with such interactions provides, at least indirectly, a measure of the shape and spatial extent of the ligand orbitals involved.

The effect of orbital perturbations upon negative ion state energies is illustrated in Figure 3 by a comparison of the electron transmission spectra of benzene and *p*-bis(dimethylamino)benzene. Benzene has three unoccupied π^* orbitals: a degenerate pair giving rise to the resonance with obvious vibrational structure near 1.1 eV and a higher energy orbital yielding a resonance at 4.8 eV. Of the degenerate pair, one is antisymmetric (A) and the other symmetric (S) with respect to the 1,4-axis. Substitution lifts the degeneracy of this pair and, as can be seen, the symmetric orbital, $\pi^*(\text{S})$, is destabilized as a result of a resonance interaction with the nitrogen 2p of the substituent.

Very often in the spectra of the substituted benzenes a resonance associated with a substituent-based molecular orbital appears. We believe this orbital to be the M-C σ^* orbital analogous to the orbital responsible for the resonance in the $\text{M}(\text{CH}_3)_m$ compounds of the previous section. Figure 4 shows the σ^* resonance in *p*-bis(dimethylphosphino)benzene in comparison to the analogous σ^* resonance in trimethylphosphine. All of the available data on the para-disubstituted benzenes are assembled in Figure 5.^{15,16,25} This diagram is intended to suggest the correlation between anion-state energies and the relevant molecular orbitals.

For the benzenes carrying group 14 element substituents,¹⁵ the anion state associated with electron capture into the σ^* orbital is denoted σ_{π}^* since this orbital is of the correct symmetry to interact with the symmetric π orbitals in benzene, as the data indicate it does. For the Si, Ge, and Sn compounds this interaction leads to a stabilization of $\pi_4^*(\text{S})$, the magnitude of which is modified by the increasing bond length from the benzene carbon to the central substituent atom on going from Si to Sn.²⁶ In addition, the stabilization in the energy of the resonance associated with σ_{π}^* results

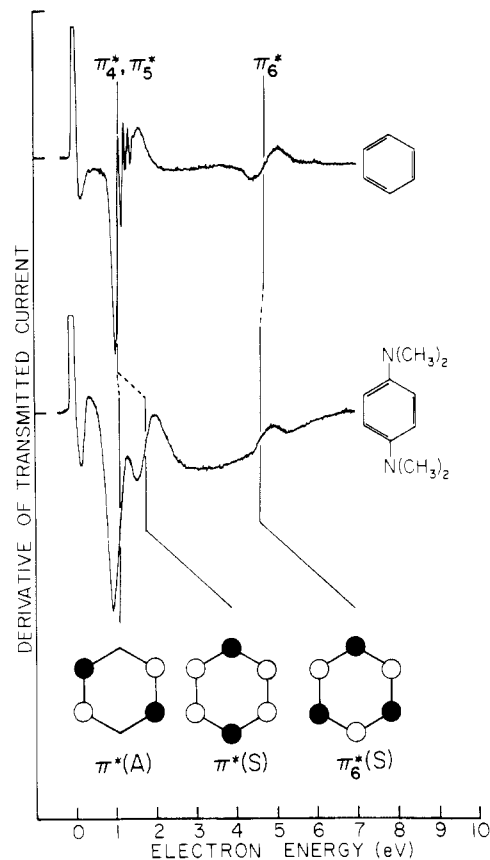


Figure 3. Derivative electron transmission spectra of benzene and *p*-bis(dimethylamino)benzene illustrating the perturbation of benzene π^* orbitals by orbitals localized on the substituent.

in a crossing in π_6^* and σ_{π}^* down the group.

For the group 15 and 16 compounds¹⁶ in which the central atom of the substituent comes from the first row of the periodic table (i.e., N and O), the dominant influence on the energies of π_4^* and π_5^* is the destabilizing interaction between the symmetric benzene orbital and the occupied 2p orbital on N or O. Hence $\pi^*(\text{S})$ for these compounds is destabilized with respect to its energy in benzene. The σ_{π}^* resonance in these compounds is above the π_6^* resonance.

By contrast to the benzenes containing first row substituents, those with $-\text{P}(\text{CH}_3)_2$, $-\text{As}(\text{CH}_3)_2$, or $-\text{SCH}_3$ substituents show the effect of a stabilizing inductive interaction. This is most pronounced in *p*-bis(methylthio)benzene, where the π_4^* and π_5^* resonances are about 0.6 eV lower than in the unsubstituted benzene, and there is no splitting of the resonances. The σ_{π}^* resonance in the P and As compounds lies well below π_6^* suggesting that the corresponding σ^* orbital should be available for back-bonding. Reference to the π -acceptor series above confirms this supposition. The σ^* resonance in *p*-bis(methylthio)benzene is likewise quite low in energy, but, since the S-C bond of the $-\text{SCH}_3$ group lies in the plane of the benzene, there is no possibility of an interaction of the methylthio σ^* orbital with the benzene π system. Modelli et al. have pointed out that, for $-\text{SR}$ groups where R is larger than the methyl group, the S-C bond is not in the plane and the possibility of a π interaction exists. Indeed, the effect of this interaction can be observed in ETS.²⁷

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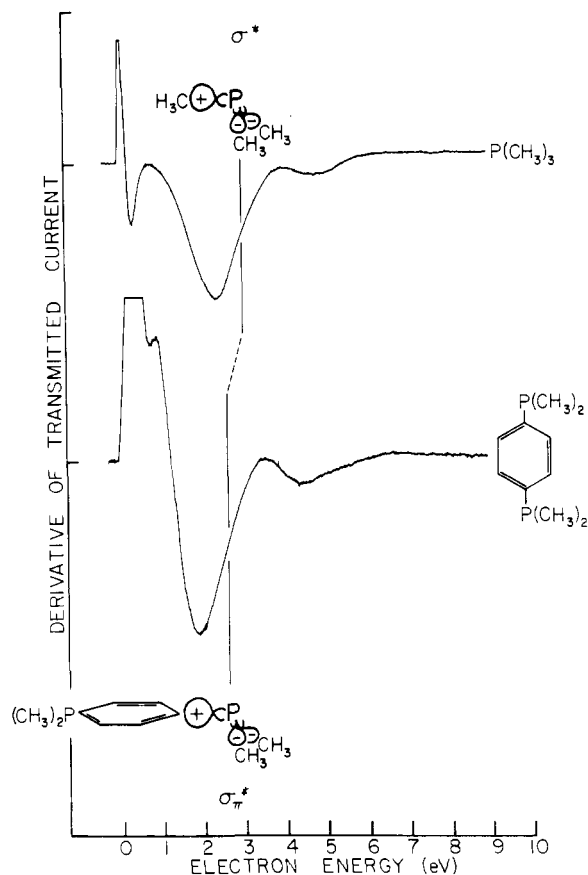


Figure 4. Derivative electron transmission spectra of trimethylphosphine and *p*-bis(dimethylphosphino)benzene demonstrating the appearance of similar features due to analogous σ^* orbitals centered on phosphorous. A stylized representation of a σ^* orbital of e symmetry (in C_{3v}) is shown. A contour diagram of this orbital is given in ref 20.

For the group 17 para-disubstituted benzenes,²⁵ no σ - π interaction between the ligand and benzene is possible. The energies of the resonances for this series imply that the inductive effect of the halogen substituents dominates the orbital energies. Also, the inductive effect increases on going down group 17. This trend is in opposition to the electronegativity of the elements and is attributed to the increasing ability of the atoms Cl, Br, and I to accept the additional electron charge.

Transition Metal Complexes

Only a relatively small number of organometallic molecules have been studied by electron transmission spectroscopy. The range of subjects has been limited by the availability of pure samples, by problems associated with handling and with chemical decomposition in the spectrometer, and by the difficulty of interpretation of the spectra. However a series of prototypical monodentate complexes (d^6 metal carbonyls²⁸) and polydentate complexes (metallocenes^{29,30} and benzene-metal complexes³¹) have been investigated. These results should serve as a benchmark for the study of less symmetrical compounds.

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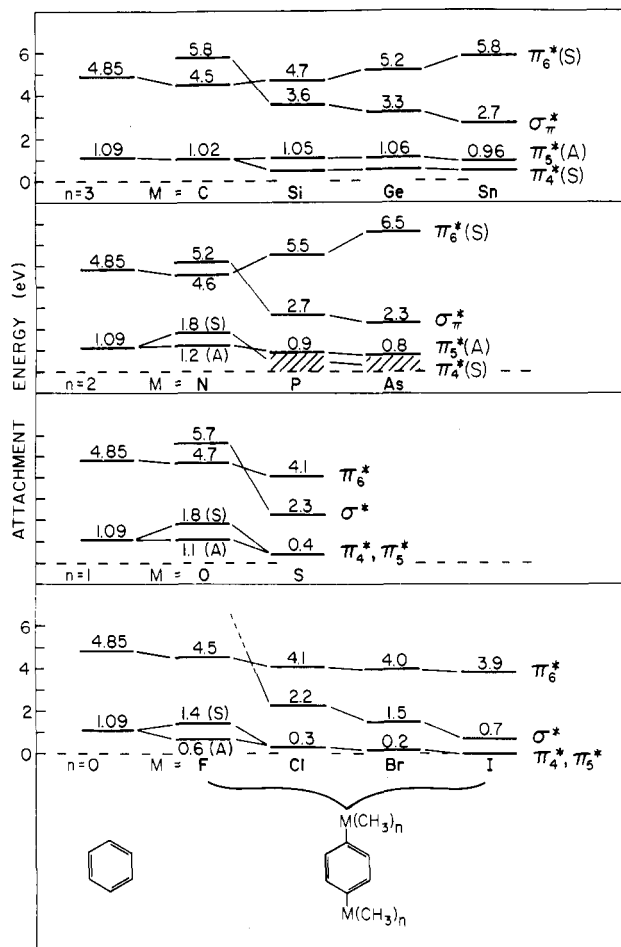


Figure 5. Correlation diagram showing electron attachment energies to unoccupied σ^* and π^* orbitals of *p*-benzenes with permethylated main-group substituents. The σ - π interaction in the group 14 and 15 compounds is obvious. Such an interaction is impossible due to symmetry in the group 16 and 17 compounds.

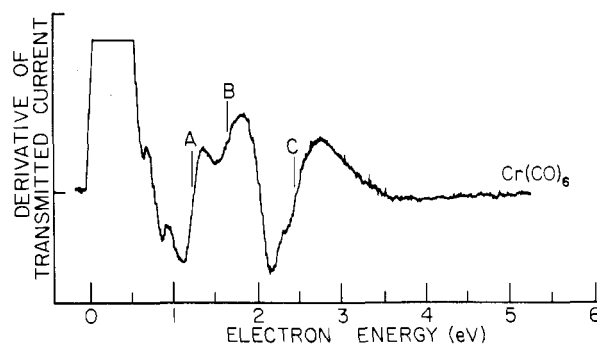


Figure 6. Derivative electron transmission spectrum of chromium hexacarbonyl.

The complexity of the spectra of organometallics is evident in the spectrum of $\text{Cr}(\text{CO})_6$ in Figure 6. This complexity prevents the use of qualitative, symmetry-based MO models for assignment of the observed electron scattering resonances. Rather, the multiple scattering $X\alpha$ (MS- $X\alpha$) method has been employed.³² This method has proven valuable for the assignment of the photoelectron and UV spectra of molecules containing transition metal atoms.³³ Early on, the bound-state version of the $X\alpha$ method was used with

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Table III.
Ground-State Electronic Configuration of Neutral
Metalloenes Along with Resonance Energies (in Parentheses)
and Calculated^a Attachment Energies for Occupation of
Low-Lying Unfilled Molecular Orbitals^b

	ground state of neutrals		calcd AE's for occupation of		
	term	electronic configuration	5a _{1g}	3e _{2g}	4e _{1g}
V(Cp) ₂	⁴ A _{2g}	(3e _{2g}) ² (5a _{1g})	0.14	0.33	1.35, 2.89 ^c (1.5)
Cr(Cp) ₂	³ E _{2g}	(3e _{2g}) ³ (5a _{1g})	-0.58 ^d	-0.19 ^d	1.14, 2.20 ^e (0.9, 2.0)
Fe(Cp) ₂	¹ A _{1g}	(3e _{2g}) ⁴ (5a _{1g}) ²			1.15 (0.6)
CO(Cp) ₂	² E _{1g}	(3e _{2g}) ⁴ (5a _{1g}) ² (4e _{1g})			0.93, -0.47 ^f (0.5)
Ni(Cp) ₂	³ A _{2g}	(3e _{2g}) ⁴ (5a _{1g}) ² (4e _{1g}) ²			-0.13 ^d (0.0)

^a Spin-polarized MS-X α with stabilization in each case except Ni(Cp)₂. ^b Mn(Cp)₂ has been ignored, partly because the ground state is unknown (ref 35). ^c Quintet and triplet states, respectively. ^d Negative attachment energy implies a stable anion state. ^e Quartet and doublet states, respectively. ^f Singlet (¹A_{1g} + ¹E_{2g}) and triplet (³A_{2g}) respectively.

a stabilization technique that involves enclosing the anion in a spherical shell of charge.²⁸⁻³⁰ Recently, continuum MS-X α calculations of elastic electron-scattering cross sections³⁴ have been employed.

The metallocenes have been the subject of electron attachment studies. Our observations,²⁹ along with those of Modelli et al.,³⁰ comprise an almost complete set of data on the 3d metallocenes. Some of the experimental observations along with the predictions from X α calculations for the energies of anion states arising from occupation of low-lying unoccupied molecular orbitals are assembled in Table III. It is noteworthy that the calculations appear to be within 0.5 eV of experimental observation. A prominent feature is the resonance associated with occupation of the predominantly metal 3d, 4e_{1g} molecular orbital. The attachment energy for the 4e_{1g} decreases across the series as expected from the lowering of the average 3d-orbital energy with increasing atomic number. This decrease is modulated by the destabilizing effect of the cyclopentadienyl group. A decreasing metal-to-ring distance³⁶ slows the decrease of the 4e_{1g} energy from V to Fe and an increasing metal-to-ring distance hastens the decrease from Fe to Ni.

Furthermore, both theory and experiment suggest that the ground state of the vanadocene anion and the ground state and first excited state of the chromacene anion are stable. The spin splitting, especially in the high spin complexes, is seen to be quite large. Finally, although definite assignments have not been made, it is clear from the calculations that resonances observed in the 2-3 eV range can be assigned to electron capture into molecular orbitals of cyclopentadienyl π^* character.

Electron transmission spectra of the metal carbonyls, as exemplified by the spectrum of Cr(CO)₆ in Figure 6,

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are quite complicated and still await a complete theoretical understanding. MS-X α calculations with stabilization appear to predict attachment energies slightly lower than actually observed.²⁹ On the other hand, restricted Hartree-Fock calculations³⁷ predict the first anion state to be 1.5 eV above threshold although there are clearly attachment processes occurring near 0.0 eV as can be seen from the electron transmission spectrum at threshold, as well as the observation of dissociative attachment of electrons of essentially 0 eV energy. It is obvious now that the bound state approach must be applied with caution when dealing with a metal complex with closely spaced orbitals of very different character. In the case of Cr(CO)₆ the continuum MS-X α method has recently been employed with some success.³⁸

In the d⁶ metal carbonyls several features below 1 eV in the electron transmission spectra are associated with electron capture into various metal-based ligand-field orbitals. In fact, both theory and experiment suggest that the ground state of the anion may be stable. The next resonance, near 1.5 eV (feature A in Figure 6), is primarily associated with the t_{2u} (CO 2 π) molecular orbital. Above this lies a resonance associated with the e_g(CO 6 σ) orbital followed by a broad resonance which we associate with a number of other ligand-based molecular orbitals.

Concluding Remarks

Electron transmission spectroscopy can be used to investigate anions arising from electron capture into low-lying, unoccupied molecular orbitals. In general, the electron transmission spectra of group 14-16 compounds display a feature associated with a σ^* orbital of the appropriate symmetry to interact in a π fashion with a metal center. In first row compounds of C, N, and O, it is evident that this σ^* orbital is too high in energy to be involved in d _{π} -p _{π} interactions. For ligands containing atoms below the first row, inductive stabilization of this σ^* orbital accounts for their π -acceptor ability.

By measuring and analyzing the electron attachment energies of related series of ligand systems and highly symmetrical transition metal complexes, a basis is provided for understanding the nature of the unoccupied ligand orbitals involved in electron back donation from a metal center. These data, in conjunction with energy measurements from PES and UV experiments, help complete a picture of the properties of the valence orbitals in organometallic, ligand, and ligand-model compounds. Projecting optimistically into the future, we suggest that it may be possible to employ such observations along with quantum mechanical calculations to predict the π -acceptor strength and lability of ligands.

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