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EXPERIMENTAL INVESTIGATION OF THE IONIZATIONS,
ELECTRONIC STRUCTURE, AND BONDING OF
SMALL MOLECULES ATTACHED TO TRANSITION METALS

MASTER

PROGRESS REPORT
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Dennis L. Lichtenberger
University of Arizona
Tucson, Arizona 85721

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ABSTRACT

Progress in the experimental investigation of the electron distribution and bonding of small molecules with transition metals is reported. The experimental methods being developed are high resolution valence ionization (photoelectron) spectroscopy utilizing HeI and HeII ultraviolet excitation sources and core level ionization spectroscopy utilizing x-ray excitation sources. These methods are being developed for detailed examination of species in the gas phase containing metal interactions with small molecules and molecular fragments that are important to catalysis and surface chemistry. Breakthroughs have been made in observation of metal-ligand and metal-metal vibrational fine structure in predominantly metal valence ionizations. Another important discovery, made possible by the development of gas-phase x-ray photoelectron spectroscopy for higher temperatures, is that the metal and ligand core ionizations shift in unison with valence nonbonding atomic orbital ionizations. Specific results are presented for more than twenty-five systems that have been investigated, including carbonyls, vinylidenes, nitrosyls, thionitrosyls, alkyls, halogens, cyanide, and sulfur dioxide bound to transition metal centers.

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I. INTRODUCTION

During the past twelve months we have made substantial progress in developing experimental methods for the study of the electronic structure and bonding in organometallic molecules. We have gained much practical knowledge from the application of these methods to the study of transition metals interacting with small inorganic and organic species, including carbonyls, olefins, methylenes, vinylidenes, nitrosyls, thionitrosyls, alkyls, halogens, cyanide, and sulfur dioxide. Also included in these studies are various methyl substituted cyclopentadienes and benzenes.

Our research focuses on high resolution valence HeI/HeII UPS and core XPS of organometallic molecules in the gas phase. We are the only group to have demonstrated the ability to observe metal-ligand vibrational fine structure in the predominantly metal ionizations of several of these molecules. The frequency and intensity distribution of this fine structure gives direct information on the role of an electron in these orbitals in binding and activating the coordinated molecule. In this report we also announce observation of metal-metal vibrational fine structure in the "delta" ionization of quadruply-bonded dimers. The HeII experiments are important to this research because the relative cross-sections for the observed bands provide experimental information on the metal character of the ionizations. The gas phase core XPS experiments have proven to be especially informative and valuable. We have found that the metal core ionizations shift consistently and by a very similar amount with metal valence nonbonding orbital ionizations. Thus both the core and the nonbonding valence ionizations consistently reflect the charge

distribution around the metal. Other metal valence orbitals that are bonding (or antibonding) with coordinated molecules shift both because of the charge distribution and, in addition, because of orbital overlap interaction with the ligands. Thus the core ionization shifts can be used to separate charge distribution effects from bonding effects in the valence ionizations. This has proven to be essential in definitively understanding the electronic structure and stability of these metal-molecule interactions, and is an area in which we are excited about further exploration.

Many of the details of this progress report are available in papers in the literature or in the form of preprints of publications. Below are briefly outlined some of the developments in instrumentation (Section II) and what we have learned from application of these techniques to significant metal-molecule interactions (Section III).

II. INSTRUMENT DEVELOPMENTS

In last years report we demonstrated several ways in which our instrumentation is unique for these investigations. We have continued to make significant improvements and developments in the instrumentation and have furthered expanded our capabilities.

A. Data Analysis Computer. The interfacing of our photoelectron spectrometer to a fully dedicated LSI-11/23 computer with "state-of-the-art" digital to analog converters, etc., has greatly increased the efficiency of data collection procedures and the quality of the data we are able to obtain. The need for this equipment was discussed in last year's budget justification. In high resolution HeI work (particularly for observation of vibrational fine structure as described in last years report) this means that complete data analysis can be carried out at the time of data collection, including derivative and Fourier Transform analysis. For XPS work peak positions are quickly and precisely determined on-line enabling the operator to closely monitor the experiment as it proceeds. Overall, the new data analysis system not only saves research time during and after data collection, but also helps minimize the amount of sample used, thus saving synthesis time and material costs.

B. The construction of a new gas phase XPS cell now allows us to obtain XPS data for samples which sublime at temperatures as high as 250 C. This extends our XPS range to match our existing UPS range. To our knowledge we are the only laboratory in this country with gas phase XPS capability in this range. We are currently involved in studies on the core ionizations of metal-metal quadruple bonded systems in the 220-250 C range.

III. RESEARCH RESULTS.

A. The Electronic Structures of Bridging Vinylidenes.

In last years report we described the study of the HeI photoelectron spectrum and theoretical analysis of a methylene group bridging between two manganese centers in a dicarbonyl-cyclopentadienyl-manganese dimer molecule. We have shown previously that the "fluidity" of the electron distribution in such systems can be determined from examination of the ionization shifts caused by different degrees of methylation of the cyclopentadienyl ligands. Herrmann reports that the pentamethyl-cyclopentadiene analogue of the methylene complex has eluded synthesis. However, a vinylidene complex analogous to this methylene complex has been reported, and we have been successful in preparing a series of vinylidene complexes with 0, 1, and 5 methyl groups on the cyclopentadienyl rings. The vinylidene pi bond also offers an additional probe of the electron distribution. A systematic characterization by gas phase HeI/HeII UPS and gas phase XPS of these complexes, as well as by approximate molecular orbital calculations, was carried out. Identification of the spectra was aided by comparison with the ionizations of $((\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))\text{Mn}(\text{CO})_3$, $((\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))\text{Mn}(\text{CO})_2\text{C}_2\text{H}_4$, and $\eta\text{-CH}_2\text{-}((\eta^5\text{-C}_5\text{H}_4(\text{CH}_3)\text{Mn}(\text{CO})_2)_2$ from our earlier work. It is found that the interaction of the vinylidene with the metal is also mainly carbene in nature. The pi ionization of the carbon-carbon double bond in the vinylidene (8.9 eV for the Cp complex) is unusually low. The x-ray structure of the complex indicates that this is not because of weakening or interaction of the double bond with the metals. Rather, the core ionizations and calculations show that this destabilization is caused by a large negative charge on

the coordinated carbon atom, a result which is consistent with our earlier studies of the methylene complexes. The formation of the net metal-metal bond is also again found to be an important factor in the stability of the complex.

B. Cyclopentadienyl Ring Distortion in $(\eta^5\text{-C}_5(\text{CH}_3)_5\text{Rh}(\text{CO})_2$.

Comparison of the valence ionization spectra of $(\eta^5\text{-(CH}_3)_5\text{C}_5\text{H}_5\text{-}\eta)\text{M}(\text{CO})_2$ (where $\text{M}=\text{Co}$ and Rh and $n=0$ and 5) indicates that the cyclopentadienyl ionizations of the rhodium complexes differ significantly from the cobalt analogs, particularly in the splitting of the e_1'' ring ionizations. An X-ray crystallographic study of $(\eta^5\text{-CH}_3)_5\text{C}_5\text{Rh}(\text{CO})_2$, I, was undertaken in order to discern any cyclopentadienyl structural differences which would lead to such significant e_1'' ring ionization changes. The results clearly reveal a ring distortion of two-fold (mirror plane) symmetry similar to the cobalt analog. Semi-empirical molecular orbital calculations on an idealized $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$, in which the ring is given D_{5h} symmetry, illustrate the origin of this distortion in the ring. The calculated 3-dimensional electron density maps show that the bonding of the ring to the metal is slightly dominated by a "dialkene" type interaction in which a single e_1'' orbital of the ring donates into an empty in-plane dxz -type orbital of the d^8 $\text{Rh}(\text{CO})_2$ portion of the molecule. The distortions of the ring are consistent with the character of this orbital. The actual cyclopentadienyl ring distortions in I, however, do not differ significantly from those in the ring of the cobalt analog, supporting our earlier proposal that the ring e_1'' ionization differences arise from changes in the relaxation energy effects rather than structural effects.

C. Vibrational Fine Structure in the Valence Ionization of Molecules Containing Metal-Metal Quadruple Bonds.

We have recently accomplished the first observation of metal-metal vibrational structure in photoionization spectra. The valence photoelectron (p.e.) spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ clearly shows resolved vibrational progressions in the first two ionization bands. These bands have previously been assigned as the predominantly metal " δ " and " π -bonding" ionizations, respectively. Evaluation of these vibrational progressions has been performed by several techniques including first-derivative, spectral simulation, Fourier transform and residuals of fit (a "manual Fourier transform") analyses. These methods consistently show the observed frequency of the progressions in the resultant positive ion ($(\text{Mo}_2(\text{O}_2\text{CCH}_3)_4)^+$) to be somewhat lower than the observed totally symmetric (alg) metal-metal stretching frequency of the neutral molecule (406 cm^{-1} , taken from reported Raman data). In particular, the δ -bonding ionization band ($2B_{2g}$ positive ion state) shows approximately 20 vibrational quanta with a frequency spacing of $360(10) \text{ cm}^{-1}$. This lowering of vibrational frequency is consistent with a reduction of formal metal-metal bond order upon loss of the $2b_{2g}$ (bonding) electron. Notably, this stretching frequency in the $2B_{2g}$ state is also lower than that observed in the $1A_{2u}$ electronically excited state, which involves excitation of one electron from the δ bonding orbital to the δ antibonding orbital. This observation provides direct evidence that the change of the metal's oxidation state upon $2b_{2g}$ ionization plays an important role in determining the strength of the metal-metal interaction. Additionally, at least 8 vibrational quanta are

observed to separate the adiabatic and vertical (most probable) ionizations. Normal Frank-Condon analysis of the progression reveals a significant metal-metal bond lengthening on the order of 0.17-0.18 angstrom in this ion state.

D. The Electronic Structure of Several SO₂ Complexes of Mn and Re.

The surprisingly similar coordinating abilities of SO₂ and CO in a series of d⁶-organotransition metal complexes have been recently documented by our gas-phase HeI, HeII (UPS), MgK alpha (XPS) valence and core ionization studies of (n-5(CH₃)nC₅H₅-n)M(CO)₂(SO₂), where M=Mn and Re and n=0,1 and 5. These ionization results when compared to the parent tricarbonyl complexes (((n-5(CH₃)nC₅H₅-n)M(CO)₃)), reveal that not only are SO₂ and CO virtually indistinguishable in their effects on the ordering and splitting of the metal valence levels, but are also nearly indistinguishable in their ability to redistribute atomic charge on the metal in this d⁶ series of complexes. These similarities are particularly surprising when one considers that CO has a low-lying degenerate pair of empty pi-accepting orbitals whereas SO₂ has only one very low-lying pi-acceptor orbital (out-of-plane) and another pi-acceptor orbital (in-plane) at relatively higher energy. The combination of sigma-donating and pi-accepting interactions of the SO₂ apparently create a bonding environment very similar to that of CO. This study has also presented us with a classic example of the importance of the "two-center effect" (point charge potential effect) in the stabilization of both core and valence orbitals. The atomic charges on the metals in these SO₂ and CO complexes are closely identical, but the metal core and valence orbitals are

stabilized by potential interactions with the large positive sulfur atom next to the metal center (two center effect).

E. Comparison of Nitrosyl to Thionitrosyl Binding in

A thorough characterization of the $CpCr(CO)NO$ and $CpCr(CO)NS$ molecules ($Cp=n5-C5H5$) by both gas phase UPS and XPS clearly reveals the electronic effects of substituting NS for NO. The HeI/HeII UPS results show the energy and orbital composition of the first ionization to be nearly the same for the two complexes. A short C-O stretching progression (2000 cm^{-1}) observed in this first band of the nitrosyl complex supports its assignment to a $2a'$ symmetry orbital, which is symmetrically delocalized into the cis carbonyls and has delta symmetry (i.e., non-bonding) to the NO or NS ligand. The next ionizations for both complexes can be assigned to the $1a'$ and a'' symmetry orbitals which are of Cr-NO or Cr-NS pi symmetry. These levels are nearly degenerate in the nitrosyl complex and stabilized nearly 1 eV relative to the $2a'$ by strong Cr-NO backdonation. For the NS complex the $1a'$ and a'' are partially resolved and destabilized (relative to the nitrosyl case) due to considerable interaction of the filled $1a'$ and a'' levels of the $CpCr(CO)_2$ fragment with the filled NS pi bonding levels. The dramatic HeII reduction of the combined $1a'$ and a'' band area for the thionitrosyl complex demonstrates significant NS (sulfur) character for these orbitals. A N 1s binding energy for the thionitrosyl complex almost 2 eV lower than that for the NO complex suggests a much more negative charge on the NS nitrogen atom, while the $CpCr(CO)$ core binding energies do not differ significantly between

the two complexes. The results of a formal Potential Model analysis of the (Cr-N-O) and (Cr-N-S) XPS shifts together with the valence results show greater metal electron delocalization for the NS complex from both NS sigma donor and pi acceptor character mixing with the CpCr(CO)_2 a'' and $1a'$ levels. A slightly more positive metal in the NS complex is also in agreement with Fenske-Hall approximate calculations and with the qualitative interpretation of the carbonyl infrared shifts between the two compounds.

F. The Electronic Structure of $\text{XW(CO)}_4\text{NO}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$).

The tungsten-nitrosyl-halide complexes, $\text{trans-X-W(CO)}_4\text{NO}$, provide a convenient format for comparing the W-NO interaction with the isoelectronic Re-CO interaction found in the X-Re(CO)_5 complexes. The metal $d_6 t_{2g}$ level of the parent hexacarbonyl system is observed to split into an e and a b_2 symmetry level for the X-Re(CO)_5 and $\text{trans-X-W(CO)}_4\text{NO}$ C_{4v} complexes. The b_2 level of several of the Re and W complexes shows a short C-O stretching progression indicating significant delocalization into the four equatorial carbonyls. The replacement of a carbonyl by a halide (transforming M(CO)_6 to XM(CO)_5 causes the metal e level to be 0.5eV less stable relative to the b_2 level in the case of the X-Re(CO)_5 complexes. For the $\text{X-W(CO)}_4\text{NO}$ complexes; the metal b_2 and e levels are very close in energy, showing the strong stabilizing influence of the nitrosyl ligand on the metal e levels. This e stabilization gives rise to a significant reduction in metal-halide pi mixing in going from the trans-X-Re-CO group to the isoelectronic X-W-NO group. This is consistent with the stronger pi acceptor nature of the NO ligand removing available metal d pi density away

from the halide atom. The XPS data shows the oxygen 1s ionization of the NO ligand shifted to nearly 2 eV lower binding energy than the CO ligands (approximate 4:1 ratio), again demonstrating the strong pi electron withdrawing power of the nitrosyl ligand. The ease of CO dissociation from the $X-W(CO)_4NO$ complexes can be attributed in part to the strong NO withdrawal of metal d-pi density, which substantially weakens the bonding to the four equatorial carbonyls.

G. The Electronic Structure and Bonding in the $CpFe(CO)_2X$ and $CpCr(NO)_2X$ Complexes (X = halide, CH_3 , CN).

We have now completed an exhaustive UPS/XPS analysis on those isostructural and isoelectronic d6 dinitrosyl and dicarbonyl systems. In a manner similar to that described for the $X-Re(CO)_5/X-W(CO)_4NO$ complexes, a significant reduction in metal-halogen pi orbital mixing is noted in the dinitrosyl complexes. Interestingly, the data from the methyl complexes reveals that the increased stability of metal-(NO)₂ d pi levels from $Fe-(CO)_2$ to $Cr-(NO)_2$ is accompanied by a marked destabilization in the corresponding metal- CH_3 sigma bond levels, as well as the Cp ring-metal sigma ionizations. The cyano complexes also show the increased metal d pi stability for the $Cr-(NO)_2$ system, but only slight destabilization of the corresponding Cr sigma levels. The reduction in sigma destabilization observed from $CpFe(CO)_2CN$ to $CpCr(NO)_2CN$ illustrates the weaker sigma donating ability of CN compared to that CH_3 . Our observation of the destabilization of the metal- CH_3 sigma bond from $CpFe(CO)_2CH_3$ to $CpCr(NO)_2CH_3$ can be directly correlated to the higher reactivity (noted by Wojcicki and co-workers) of the $CpCr(NO)_2-R$ (alkyl, aryl, propargyl) complexes towards electrophiles.

IV. PERSONNEL

Principal Investigator: Dr. Dennis L. Lichtenberger

Department of Chemistry, University of Arizona

The P. I. was promoted to Associate Professor during this period. He devoted 100% of his time during 11 summer weeks to this project and at least 25% of his time during the academic year to actively direct and perform research under this project.

Students:

Dr. David C. Calabro studied olefin and methylene interactions with metals during this period. He received his Ph.D. in December 1981 and is presently on the research staff at Mobil.

Mr. John L. Hubbard developed the gas phase HeI and HeII UPS, and the gas phase XPS capabilities for the instrumentation. His research involves investigation of the ionizations and electronic structure of organometallic carbonyl, nitrosyl, thionitrosyl, alkyl, halide, and cyanide complexes. During this past year he has been awarded the Marvel Fellowship for the outstanding research in this Department.

Mr. Charles H. Blevins III investigated the metal-metal vibrational fine structure in the delta ionization of quadruply bonded complexes, the bonding interactions of SO₂ with metals, and structural aspects cyclopentadienyl coordination in organometallic molecules. He won one of three summer fellowships in this Department on the basis of his continuing work, and was supported during the academic year from this grant.

Mr. Louis S. K. Pang investigated a series of bridging vinylidene and methylene complexes. His support was 100% from this grant.

Mr. Glen E. Kellogg interfaced the new computer and data analysis system to the instrument. He was paid totally by the Department for operation and maintenance of the instrumentation.

Mr. John Coffey, an undergraduate, was very helpful in the summer months in preparing a number of organometallic molecules. In the coming summer he is prepared to assume responsibility for his own research project.

V. NEW PUBLICATIONS

1. The Jahn-Teller Effect in the Photoelectron Spectrum of Iron Pentacarbonyl. John L. Hubbard and Dennis L. Lichtenberger, J. Chem. Phys., 75, 2560 (1981).
2. The Effects of Methyl Group Substitution on Metal-Coordinated Cyclopentadienyl Rings. The Core and Valence Ionizations of Methylated Tricarbonyl-eta-5-cyclopentadienylmetal Complexes. David C. Calabro, John L. Hubbard, Charles H. Blevins III, Andrew Campbell, and Dennis L. Lichtenberger, J. Am. Chem. Soc., 103, 6839 (1981).
3. Valence Ionizations of Olefins Coordinated to Metals. Olefin Dicarbonyl-eta-5-(methyl-and pentamethyl-cyclopentadienylmanganese Complexes. David C. Calabro and Dennis L. Lichtenberger, J. Am. Chem. Soc., 103, 6846 (1981).
4. The Valence Electronic Structure of Bridging Methylenes: U.V. Photoelectron Spectroscopy of mu-methylenebis (dicarbonyl-eta-5-cyclopentadienylmanganese). David C. Calabro, Dennis L. Lichtenberger, and W. A. Herrmann, J. Am. Chem. Soc., 103, 6852 (1981).
5. Comparative Studies of Mo-Mo and W-W Quadruple Bonds by SCF-Xa-SW Calculations and Photoelectron Spectroscopy. F. A. Cotton, J. L. Hubbard, Dennis L. Lichtenberger, and I. Shim, J. Am. Chem. Soc., 104, 679 (1982).
6. Vibrational Fine Structure in the Valence Ionizations of Transition Metal Hexacarbonyls: A New Experimental Indication of Metal-to-Carbonyl pi-bonding. J. L. Hubbard and Dennis L. Lichtenberger, J. Am. Chem. Soc., 104, XXXX (1982).

VI. TALKS PRESENTED AT MEETINGS

1. Instrumentation and Applications of Gas Phase Photoelectron Spectroscopy. J. L. Hubbard and Dennis L. Lichtenberger, American Vacuum Society, Arizona Chapter, Scottsdale, February, 1981.
2. Unusually Large Changes in the Valence Ionizations of First and Second Row Transition Metal-Cyclopentadienyl Carbonyl Complexes. D. C. Calabro and Dennis L. Lichtenberger, A.C.S. National Meeting, New York, August 1981.
3. Experimental Analysis of Charge Distribution and Electronic Structure of $\text{CpCr}(\text{CO})_2\text{NO}$ and $\text{CpCr}(\text{CO})_2\text{NS}$. J. L. Hubbard and Dennis L. Lichtenberger, A.C.S. National Meeting, New York, August, 1981.

4. Vibrational Fine Structure in the Valence Ionization of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. C. H. Blevins III and Dennis L. Lichtenberger. Pacific Conference on Chemistry and Spectroscopy, Anaheim, October, 1981.
5. The Valence Electronic Structure of Bridging Vinylidene Complexes: HeI/HeII UPS of Study $(\mu\text{-CCH}_2)((\eta^5\text{-C}_5\text{H}_5\text{-n}(\text{CH}_3))\text{n Mn}(\text{CO})_2))_2$ ($\text{n}=0,1,5$). Dennis L. Lichtenberger and Louis Pang, 183rd A.C.S. National Meeting, Las Vegas, April, 1982.
6. Preparation and Molecular Structure of 1,4,7-Trithiacyclononane Molybdenum Tricarbonyl. M. T. Ashby and Dennis L. Lichtenberger, 183rd A.C.S. National Meeting, Las Vegas, April 1982.
7. Gas Phase Core and Valence Ionization Studies of SO_2 Coordinated to Metals. The Electronic Structure and Metal-Sulfur Dioxide Bonding Interactions of Some d6 Transition Metal- SO_2 Complexes. Charles H. Blevins III, Andrew C. Campbell, Dennis L. Lichtenberger, 183rd A.C.S. National Meeting, Las Vegas, April, 1982.
8. The Electronic Structure of d6 Transition Metal-Cyanide Complexes: The Bonding in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CN}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{CN}$. Dennis L. Lichtenberger and John L. Hubbard, 183rd A.C.S. National Meeting, Las Vegas, April, 1982.

VII. MANUSCRIPTS IN PREPARATION

1. Core and Valence Ionizations of Bridging Vinylidenes: Gas Phase XPS and UPS Study of μ -Vinylidene-bis (dicarbonyl- η -5-cyclopentadienyl and methylated cyclopentadienyl) manganese. Louis S. K. Pang and Dennis L. Lichtenberger.
2. Molecular and Electronic Structural Analysis of (η -5-pentamethylcyclopentadienyl)dicarbonylrhodium: Cyclopentadienyl Ring Distortions in Organo-metallo-carbonyl Species. Charles H. Blevins III and Dennis L. Lichtenberger.
3. Core and Valence Ionization Studies of SO_2 Coordinated to Metals. Charles H. Blevins III, Andrew C. Campbell, and Dennis L. Lichtenberger.
4. Vibrational Fine Structure in the Valence Ionizations of Complexes with Metal-Metal Bonds. I. The "Delta" Ionization of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Charles H. Blevins III and Dennis L. Lichtenberger.

5. The Comparison of Nitrosyl and Thionitrosyl Binding in Dicarbonyl(η^5 -cyclopentadienyl)(nitrosyl)Chromium and Dicarbonyl(η^5 -cyclopentadienyl)(thionitrosyl)Chromium by Gas Phase Ultraviolet and X-ray Photoelectron Spectroscopy. John L. Hubbard and Dennis L. Lichtenberger.
6. The Electronic Structure and Bonding in the (η^5 -C₅H₅)Cr(NO)₂-X Complexes (X=Cl,Br,I,CH₃,CN) and their (η^5 -C₅H₅)Fe(CO)₂-X Analogs by Gas Phase HeI/HeII Valence and MgK α Core Photoelectron Spectroscopy. John L. Hubbard and Dennis L. Lichtenberger.
7. The Electronic Structure and Bonding in the trans-XW(CO)₄NO Complexes (X=Cl,Br,I) by Gas Phase U.V. and X-ray Photoelectron Spectroscopy. John L. Hubbard and Dennis L. Lichtenberger.