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CHEMICAL ACTIVATION OF MOLECULES BY METALS: EXPERIMENTAL STUDIES OF ELECTRON DISTRIBUTIONS AND BONDING

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SUMMARY

During this period of the project we have (1) developed the fundamental relationships between ionization energies and bond energies in molecules, (2) examined experimentally the electronic factors of carbon-hydrogen bond activation by transition metals, (3) characterized several different bonding interactions of small molecules with transition metals, (4) measured the ionizations of buckminsterfullerene in thin films and in the gas phase, and examined its interaction with metals, (5) identified important features of electron transfer in main group molecules, and (6) continued to develop the experimental and theoretical methods for these studies. In the first area, the formal relationship between measured molecular ionization energies and thermodynamic bond dissociation energies has been developed into a single equation which unifies the treatment of covalent bonds, ionic bonds, and partially ionic bonds. This relationship has been used to clarify the fundamental thermodynamic information relating to metal-hydrogen, metal-alkyl, and metal-metal bond energies. We have been able to obtain a direct observation and measurement of the stabilization energy provided by the agostic interaction of the C-H bond with the metal. The ionization energies have also been used to correlate the rates of carbonyl substitution reactions of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ complexes, and to reveal the electronic factors that control the stability of the transition state. The extent that the electronic features of these bonding interactions transfer to other chemical systems is being investigated in terms of the principle of additivity of ligand electronic effects. Specific examples under study include metal-phosphines, metal-halides, and metallocenes. Especially interesting has been the recent application of these techniques to the characterization of the soccer-ball shaped C_{60} molecule, buckminsterfullerene, and its interaction with a metal surface. The high-resolution valence ionizations in the gas phase reveal the high symmetry of the molecule, and studies of thin films of C_{60} reveal weak intermolecular interactions. Scanning tunneling and atomic force microscopy reveal the arrangement of spherical molecules on gold substrates, with significant delocalization of charge from the metal surface. Further developments in the instrumentation and methods of gas phase and surface photoelectron spectroscopy are underway. Most notable is the progress on the new gas phase photoelectron spectrometer that combines improved capabilities for He I/He II UPS, XPS, and Auger investigations of organometallic molecules.

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CONTENTS

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I. INTRODUCTION

The research in this project has been increasingly successful and rewarding during the present funding period. As one indication of the growth of the program, the number of publications and presentations of new work has continued to increase. In fact, the number of papers that appeared in print during this period is more than twice the number that appeared in the previous period of the program. Nearly a third of the papers were published in the *Journal of the American Chemical Society*. This productivity is continuing to increase, as evidenced by the progress in the projects presently underway, the progress in construction of our second and much improved instrument for gas phase photoelectron spectroscopy, and our breakthroughs with scanning tunneling microscopy for the thin film studies. There are also several new students, postdoctorals, and visiting faculty who are contributing to the research. More important than the quantity of the work, there has been an increasing impact of the work on current problems and areas of research in basic energy sciences. This progress has led to numerous invited presentations, book chapters, and journal papers (Metal-Metal Bonds and Clusters in Chemistry and Catalysis, J.P. Fackler, Jr., Ed.; Polyhedron; Inorganometallic Chemistry, T. P. Fehlner, Ed.; Bond Energies and Thermodynamics of Organometallic Reactions, T. Marks, Ed.). We are also interacting with an increasing number of other researchers and laboratories, as others learn of the unique information we are able to obtain and the importance of this information to understanding the energetics of chemical behavior. Some of these interactions are listed in section VI, B.

This report reviews some of the accomplishments of this research program during the most recent period of this project. Brief summaries are provided in section II of selected results that have been published in the literature during this period. The results presented here point to some interesting and important investigations in the next phase of this project. The accompanying renewal proposal details some additional preliminary results and the goals and methods for these investigations in the next period of support.

II. SELECTED SUMMARIES

A. FUNDAMENTAL ELECTRONIC STRUCTURE AND BONDING INFORMATION FROM MOLECULAR IONIZATION ENERGIES.

Several studies are directed at developing the experimental information that is available from different electron spectroscopies, and understanding how this information is related to the electron distribution, bonding modes, thermodynamic bond energies, and reaction pathways of organometallic molecules. One of the more significant aspects of progress in the present period is the investigation of more direct formal relationships between ionization data and the thermodynamics of metal-assisted chemistry and catalysis. Following are some brief summaries and abstracts of publications that have appeared during the most recent funding period. Additional information and references should be obtained from the publications.

1. **Ionization Energy-Bond Energy Relationships in Organometallic Chemistry.** D.L. Lichtenberger and A.S. Copenhaver, in *Bonding Energetics in Organometallic Compounds*, Marks, Tobin J., Ed., A.C.S. Symposium Series, 428 (1990).

One of the most fundamental physical properties of atoms that serves as the basis for the understanding of chemical behavior is the ionization energy. Periodic trends in ionization energies and the relationships with the electron configurations of atoms are commonly presented in general chemistry courses. The relationships with bonding concepts such as electronegativity and the stability of ionic solids through the Born-Haber cycle are also well known. Less well known are the relationships of atomic and molecular ionization energies to the strengths of covalent bonds, where energy cycles similar to the Born-Haber cycle for ionic compounds may also be constructed. The relationships between ionization energies and bond energies are implicated in numerous photoelectron investigations. The foundations of these relationships have been developed more explicitly in this review article. The quantitative accuracy and limitations of using ionization energies to obtain bond dissociation energies are illustrated with results on single- and multiple-bonded diatomic molecules. The principles that emerge from this analysis are then used to evaluate the bond energies in $Mn_2(CO)_{10}$, $Mn(CO)_5H$, $Mn(CO)_5CH_3$, $Cp_2Nb(CO)CH_3$ and $Cp_2Nb(CO)H$. The ionization energies are particularly useful because of their direct relationships to other thermodynamic quantities through energy cycles, and can be used as a check of other thermodynamic information. In some cases, bond energy information may be obtained from the ionization energies which is difficult to measure by other chemical or thermodynamic methods. The technique has the further advantage that it allows separation of individual symmetry orbital or electron distribution contributions to the total bond. These relationships provide a unified approach to teaching the concepts of both ionic and covalent bonds.

2. **Separation of σ and π Bonding Effects in (η^5-C_5H_4X)Rh(CO)$_2$ Compounds Using Photoelectron Spectroscopy. Relating Valence Ionizations and Rates of CO Substitution.** D.L. Lichtenberger, S.K. Renshaw, F. Basolo and M. Cheong, *Organometallics*, **10**, 148-156 (1991).

The He I photoelectron spectra for a series of monosubstituted (η^5-C_5H_4X)Rh(CO)$_2$ compounds have been obtained (where **X** = NO_2, CF_3, Cl, H, CH_3, or $N(CH_3)_2$). The complexes undergo substitution of a carbonyl by phosphines and other ligands via an associative mechanism. In general, the associative substitution reactions are inhibited by greater electron richness at the metal center. However, the rates of certain reactions, particularly when X is Cl or NMe_2, are faster than indicated by the usual inductive characteristics of these groups. The photoelectron spectra of the (η^5-C_5H_4X)Rh(CO)$_2$ compounds illustrate the effects of X on the electronic structure and rates of substitution. Pronounced shifts are seen in the cyclopentadienyl π and metal d valence ionizations as the **X** group is varied. The shifts of most of the valence ionizations closely follow the inductive capabilities of the **X** substituents (as also indicated by correlations with Hammett σ values and the carbonyl stretching frequencies of the complexes). However, a few of the ionizations are also affected by **X** group orbitals that have π symmetry with respect to the cyclopentadienyl ring. Thus, the ionization energy shifts provide a relative measure of the inductive effect and the π interaction between **X** and the complex. When both the inductive and π interactions are taken into account, the rates of CO substitution correlate with the measured electronic characteristics. These results support the proposal that the rates of substitution are enhanced when the "slipped ring" intermediate (η^3-C_5H_4X)Rh(CO)$_2$PPh$_3$ is stabilized through π delocalization on the Cp ring.

3. **Delocalized Electronic Interactions in Chiral Cyclopentadienyl Rhenium Halide Complexes.** D.L. Lichtenberger, A. Rai-Chaudhuri, M.J. Seidel, J.A. Gladysz, S.K. Agbossou, A. Igau and C.H. Winter, *Organometallics*, **10**, 1355-1364 (1991).

The He I photoelectron spectra of a series of CpRe(NO)(L)X complexes (L is PPh_3 or CO; X is Cl, Br, I; Cp is η^5-C_5H_5 or η^5-$C_5(CH_3)_5$) have been obtained to help characterize this very important class of organometallic molecules. Cyclopentadienyl rhenium complexes of this type have been important in studying many aspects of the organic chemistry with transition metals. Assignment and characterization of the ionization bands is assisted by the trends in He I and He II cross-sections for ionization intensities, as well as by the widths and vibrational progressions of certain ionization bands. The shifts of the ionizations which are key to revealing the nature of the electronic structure interactions in a system, are caused by halogen substitutions on the metal, methyl substitutions on the cyclopentadienyl rings and phosphine substitutions for the carbonyls. The first three ionizations, corresponding to the three occupied d orbitals of the d^6 Re(I) metai center, are widely separated. This is because each of the three metal d orbitals have very different π interactions with the three different CO, NO and halogen ligands. The ionizations indicate extensive metal-halogen mixing and a very delocalized electronic structure throughout the metal-ligand system. The first two ionizations correspond to the metal-halogen π^* interaction which results from the filled-filled interaction, with the first ionization including backbonding to the carbonyl and the second ionization including backbonding to the nitrosyl. The third ionization involves backbonding to both the carbonyl and the nitrosyl. The first two ionizations of the iodide complexes show short vibrational progressions corresponding to the CO and NO stretches. The difference in stabilization of the metal levels by metal-carbonyl and metal-nitrosyl backbonding is determined from the splitting between the first two ionization bands. The M-X π^* orbitals have increasing halogen character from the chloride complex to the iodide complex. Unlike the previously studied $Re(CO)_5X$ complexes, where the first ionization shifted from predominantly metal to predominantly halogen in proceeding from X = Cl to X = I, in this case the first three ionizations remain predominantly metal throughout. There is indication in one case of further delocalized interaction of the M-X π electrons with Cp-based electrons. The extent of delocalized and fluid electron density in these systems is in contrast to other systems like $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ and $(CO)_5ReX$.

4. **Experimental Measures of the Electron Distribution and Bonding in bis(η^5-Cyclopentadienyl)osmium from He I and He II Valence Photoelectron Spectroscopy.** D.L. Lichtenberger and A.S. Copenhaver, *J. Chem. Phy.*, **91**, 663-673 (1989).

Metallocenes represent a fundamentally important class of organometallic complexes and have been the subject of previous investigations in this program. In a previous progress report we described a combined UPS and XPS investigation of a variety of symmetrically and unsymmetrically methyl-substituted ferrocenes. These studies have provided a new and somewhat surprising understanding of the electronic effects of methyl substitution and the electron distribution in these complexes. The He I and He II high resolution photoelectron spectra of osmocene are reported in this publication. Vibrational fine structure is observed in all the valence metal-based ionizations and in the cyclopentadienyl π ionizations which derive from the e_{1g} and e_{1u} symmetry combinations. Analysis of the vibrational progressions found in the metal-based ionizations provides a measure of the force constants and vibrational frequencies for the metal-ring stretch in the positive ions. The vibrational analysis for the $^2E_{2(5/2)}$ and $^2E_{2(3/2)}$ states of the osmocene cation (derived from the spin-orbit split ionization of the metal $e_{2g}(d_{x^2-y^2}, d_{xy})$ set) indicates a 0.12 Å greater metal-ring bond length in the cation compared to the neutral molecule. The sharp $^2A_{1(1/2)}$ ionization (correlating with removal of an electron from the metal $a_{1g}(d_{z^2})$ orbital) is observed to have a much shorter vibrational progression. The adiabatic ionization is the most intense (vertical) band of the series, indicating that there is no appreciable change in metal-ring bond distance upon ionization from the non-bonding $a_{1g}(d_{z^2})$ orbital to produce the $^2A_{1(1/2)}$ cationic state. A large spin-orbit coupling is observed in the metal ionization region and a moderate amount in the cyclopentadienyl ring π ionization region. From evaluation of the spin-orbit coupling, the ionization band which correlates primarily with the e_{1g} combination of the cyclopentadienyl π orbitals is shown to contain about 27% metal character. The spin-orbit coupling effects are negligible in the ionization which corresponds to the e_{1u} combination of the ring orbitals, as expected from the lack of symmetry interaction with the metal d orbitals. The ionizations of this complex also provide experimental measures of relative metal-based and carbon-based ionization cross-sections with He I and He II energy sources which are compared with theoretical calculations. All of the observations indicate that covalent bonding is more prevalent in osmocene than in ferrocene.

5. **Electronic Structure of Monodentate Coordinated Diphosphine Complexes.** D.L. Lichtenberger and M.E. Jatcko, *Inorg. Chem.*, accepted 08/91.

Photoelectron spectroscopy is used to study the electronic structure of molybdenum carbonyl complexes that contain diphosphine ligands bound to the metal through only one of the two phosphorus atoms. This represents the first examination of the relative bonding capabilities of diphosphine ligands in the absence of chelating geometries, which is important for understanding many chelate effects. Photoelectron spectra are reported for $Mo(CO)_5DMPE$ and $Mo(CO)_5DMPM$ and compared to the spectra of $Mo(CO)_5PMe_3$ and the corresponding free phosphine and diphosphine ligands (PMe_3 is trimethylphosphine, DMPE is 1,2-bis(dimethylphosphino)ethane and DMPM is bis(dimethylphosphino)-methane). The energy splittings between the d^6 metal-based ionizations of these complexes indicate that the π-backbonding ability is the same for each of these phosphine ligands and is relatively small, about 25% that of carbon monoxide. The metal-based ionizations shift only slightly to lower binding energy from the PMe_3 to the DMPE to the DMPM complex (total shift = 0.10 eV) due to a slightly increasing negative charge potential at the metal along this series. This would normally be interpreted as slightly increasing σ-donor strength in the order PMe_3 < DMPE < DMPM. However, the difference between the ionization energy of the coordinated lone pair (CLP) of the phosphine and the ionization energy of the lone pair of the free ligand indicates an opposite trend in σ-donor strength with PMe_3 (1.28 eV) > DMPE (1.27 eV) > DMPM (1.23 eV). The shift of the uncoordinated phosphine lone pair ionization (ULP) of the mono-coordinated diphosphine complexes, which is affected primarily by charge potential effects, reveals that the important factor is a transfer of negative charge from the uncoordinated end of the phosphine through the alkyl linkage to the coordinated phosphine. This transfer is more important for the DMPM ligand because of the shorter alkyl chain between the phosphorus atoms. Aside from these subtle details of charge distribution, the primary conclusion is that the diphosphine ligands, DMPE and DMPM, have extremely similar σ-donor and π-acceptor strengths to those of PMe_3. Studies of the electronic interactions of these ligands in chelating geometries will be reported in the next period of support of this program.

6. **The Electronic Structure of Nitrosyl and Carbonyl Supported Metal-Metal Interactions.** D.L. Lichtenberger, A.S. Copenhaver and J.L. Hubbard, *Polyhedron* Vol. 9, No. 15/16, 1783-1797 (1990).

This project is part of the extension of our investigations of small molecules bound to small metal clusters and to electron rich metal systems. This contrasts with the early to mid metals and high oxidation states in the previous studies. The valence photoelectron ionizations of $[CpFe(\mu\text{-}NO)]_2$, $[Cp^*Fe(\mu\text{-}NO)]_2$, $[CpRu(\mu\text{-}NO)]_2$ and $[Cp^*Co(\mu\text{-}CO)]_2$ ($Cp = \eta^5\text{-}C_5H_5$ and $Cp^* = \eta^5\text{-}C_5(CH_3)_5$) have been examined in comparison to several theoretical calculations of the electronic structure and bonding in these complexes. The photoelectron spectra of this group of complexes, when collected together, allow identification of the eight valence metal-based ionizations. There is considerable disparity among the various calculations on the predicted order of these ionizations. The combination of Fenske-Hall calculations with experimental observations of ionization trends between isoelectronic first row complexes (Fe(NO) vs. Co(CO)), between first and second row complexes (Fe vs. Ru), and between complexes with ring methylation (Cp vs. Cp^*) allows a consistent assignment of the valence ionizations. The interplay of theory and experiment gives unique insight into the nature of bridging ligand coordination and clarifies the relative strengths of metal-ligand and metal-metal interactions in each complex. It is found that as many metal-metal antibonding orbitals are occupied as metal-metal bonding orbitals, so that the formal metal-metal bond order is zero. The interactions are important in defining the bonding and stability of the complexes.

7. **Electronic Structure and Bonding of Buckminsterfullerene.**

Valence and Core Photoelectron Spectroscopy of C_{60}, Buckminsterfullerene, D.L. Lichtenberger, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb, *Chem. Phys. Lett.*, **176,** 203-208 (1991).

The Ionizations of C_{60} in the Gas Phase and in Thin Solid Films, D.L. Lichtenberger, M.E. Jatcko, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb, *Mat. Res. Soc. Symp. Proc*, **206** 673-678 (1991).

Modelling of the Intramolecular Structure of Monolayer C_{60} Molecules Observed with Scanning Tunneling Microscopy, T. Chen, S. Howells, M. Gallagher, L. Yi, D. Sarid, D.L. Lichtenberger, K.W. Nebesny and C.D. Ray, *Mat. Res. Soc. Symp. Proc*, **206** 721-725 (1991).

Internal Structure and Two-Dimensional Order of Monolayer C_{60} Molecules on Gold Substrate, T. Chen, S. Howells, M. Gallagher, L. Yi, D. Sarid, D.L. Lichtenberger, K.W. Nebesny and C.D. Ray, *J. Vac. Sci. & Tech.*, submitted 5/91.

Atomic Force Microscopy of C_{60} Molecules on a Gold Substrate, D. Sarid, T. Chen, S. Howells, M. Gallagher, L. Yi, D.L. Lichtenberger, K.W. Nebesney and C.D. Ray, *Applied Phys. Lett.*, submitted 6/91.

One of the most exciting recent accomplishments in the laboratory has been the acquisition of the photoelectron spectrum of C_{60}. The proposal that C_{60}, an especially stable cluster molecule of pure carbon, adopts the structure of a truncated icosahedron has sparked the imagination of many. As pointed out by Smalley, "a direct view of a molecule's electronic structure can often be best obtained from the ultraviolet photoelectron spectrum." Smalley and coworkers succeeded in obtaining the low valence photoelectron spectrum of the negative ion of C_{60}, which gave the electron affinity and an experimental measure of the separation between the highest occupied and lowest unoccupied orbitals of C_{60}. The small quantities of C_{60} produced by these experiments precluded characterization by many other common spectroscopic and chemical techniques. The laboratory synthesis and purification of C_{60} in quantities greater than 100 milligrams per day has been discovered here at Arizona by Professor Huffman. The material has been characterized by several methods (mass spectroscopy, X-ray diffraction, NMR, infrared spectroscopy, raman spectroscopy, scanning tunneling microscopy), and is now being studied by a variety of other techniques in our laboratories and elsewhere.

We have obtained the full valence and core ionization energies of neutral C_{60}. We accomplished measurement of the first photoelectron spectrum with the surface techniques we have developed for the study of metal-metal bonds. The Mg Kα X-ray (XPS) and He I/He II ultraviolet (UPS) photoelectron spectra of several thin films of C_{60} (one to three monolayers) prepared by vapor deposition on gold have been obtained. We have also obtained the scanning tunneling microscopy and atomic force microscopy images of these films. These images show the 10 Å spheres of buckminsterfullerene arranged in arrays on the surface.

The valence UPS spectra of the thin films show very sharp valence ionization bands, comparable to gas phase spectra, with wide separations between the lowest ionization energy features. Thus the electronic interactions between the molecules and with the surface do not significantly influence the molecular electronic structure or the ionizations under these conditions. The ionizations are consistent with theoretical calculations based on the highly symmetric truncated icosahedral structure, in which four-fold and five-fold degenerate levels are predicted. The high resolution He I and He II photoelectron spectra of C_{60} in the gas phase are also being examined. The spectra are obtained at 380±10°C with no evidence of C_{70} in the gas phase. The photoelectron spectra of the gas phase species are very similar in the low valence region to the spectra of thin films of C_{60} molecules on various substrates, with the exception that vibrational fine structures are observed in the first two valence ionization bands of the gas phase species. The first ionization band was examined in detail for the purpose of obtaining an accurate experimental measure of the first ionization energy. The analysis of the first band shows evidence of hot bands, and the first vertical ionization is determined to be 7.64±.02 eV. The first vertical and adiabatic ionizations coincide, but the existence of a vibrational progression indicates some geometry change of the molecule with ionization. The vibrational fine structure which is observed does not correspond to the Raman frequencies of the neutral molecule. The second ionization band is also examined in detail for evidence of the presence of two different electronic states (h_g and g_g) as predicted by theoretical calculations. The observations that the band gives a vibrational progression similar to that in the first band, and that there are no significance changes in relative intensities within the band from He I to He II excitation, indicate that the two ionizations must be very similar in energy and must also lead to very similar geometry changes in the positive ion state.

The sudden opportunity to study C_{60} in the last year was a special breakthrough that could not have been anticipated. Fortunately, the improved experimental techniques we had developed for other studies are ideally suited to the characterization of the electronic structure of this molecule. Likewise, we feel that our continuing improvements in the instrumentation for ionization spectroscopy will be important for studies of wide classes of different molecules.

B. BOND ACTIVATION IN SMALL MOLECULES BY TRANSITION METALS

In addition to building the formal theoretical relationships between ionization energies and the physical and chemical properties of small molecules attached to transition metals, we have also begun applying these principles to experimental characterization of processes of carbon-hydrogen bond activation, olefin insertion reactions, and the electronic structure of active alkyne metathesis catalysts with resulting implications on the mechanistic pathways. One of the most remarkable and important properties of transition metals is their ability to activate H-H, C-H, and C-C bonds. The primary electronic structure and bonding factors that contribute to the activation can be viewed in terms of two limiting case descriptions. The first mode of activation occurs when the C-H σ (bonding) orbital donates electron density into an empty metal level, thus weakening the C-H bond order. We refer to this interaction as σ activation. The second, which we call σ^* activation, occurs when filled metal levels donate into the empty C-H σ^* antibonding orbital, again weakening the C-H bond order. Complete breaking of the C-H bond involves both the σ and σ^* orbitals and results in oxidative addition to the metal center. Filled-filled orbital interactions can also be important in determining the pathway and energetics at different stages of the process. These interactions have been the subject of numerous theoretical investigations. The challenge remains to obtain experimental information relating to the relative energy contributions of these different interactions at different stages of the activation process.

1. Valence Photoelectron Spectroscopy of (Butenyl)tricarbonylmanganese and (Methyl-Butenyl)tricarbonylmanganese . Measurement of the Agostic Stabilization Energy.

The He I valence ionizations for (η^3-1-methylallyl)manganese tricarbonyl and (η^3-1,2-dimethylallyl)manganese tricarbonyl have been measured to help characterize the agostic interaction of a C-H bond with a transition metal center. The allyl bonding to the $Mn(CO)_3$ fragment and the agostic interaction of a methyl group C-H bond with the metal in these complexes is similar to that observed in the previous study of (cyclohexenyl)tricarbonylmanganese. The fewer C-H bonds in these acyclic complexes give rise to relatively clean C-H ionization regions, permitting observation of the agostic CH-Mn ionization as a shoulder in the vicinity of 12-13 eV. The shifts of these ionizations compared to the ionizations of the synthetic precursors (η^3-1-methylallyl)tetracarbonylmanganese and (η^3-1,2-dimethylallyl)tetracarbonylmanganese, in which the additional coordinated CO replaces the CH-Mn interaction, reveal that the agostic stabilization energy of the CH-Mn bond is approximately 0.3-0.4 eV (7-9 kcal/mol). This observation is in excellent agreement with estimates via other methods on a variety of agostic complexes and shows that the stabilization of the complex derives directly from the agostic interaction and not from other features of the bonding between the metal and the supporting ligand. Also evident from these data and comparison to the ionizations of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2P(CH_3)_3$ is that the contribution of σ^* activation (i.e. donation from the metal to the C-H σ^* orbital) is not significant to the stability of these complexes.

2. Cyclopentadienyl Ring Methylation and Its Effect on Si-H Bond Activation.

D.L. Lichtenberger and A. Rai-Chaudhuri, *J. Am. Chem. Soc.*, 112, 2492 (1990).

Complete oxidative addition of an aliphatic C-H bond to a metal center has not been investigated yet by these techniques. However, the general principles have been illustrated by our related study of Si-H bond addition to metals. A part of this project was supported by the Petroleum Research Fund in the first two years of the period. The He I photoelectron spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$ and $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HSiHPh_2$ (Ph is C_6H_5) have been compared to observe the effect of cyclopentadienyl ring methylation on the extent of Si-H bond interaction with the transition metal in these complexes. As in the case of C-H bonds, the addition of the Si-H bond to the transition metal center involves interaction of the Si-H σ and σ^* orbitals with the metal. The electron distribution between the Si-H bond and the metal is obtained by the relative stabilities of the metal-based and the ligand-based ionizations. The splitting and the intensity pattern of the metal-based ionizations of the three complexes reflect the formal d^6 electron count of a metal corresponding to a formal oxidation state of +I. The extent of electron charge density shift from the metal to the ligand is small as indicated by the small shifts of these ionizations from those of the free ligand. These observations indicate that the electronic structure of the Si-H interaction with the metal is in the initial stages of Si-H bond addition to the metal, before oxidative addition has become prevalent in these trialkylsilyl complexes. The extent of electron charge transfer from the metal to the σ^* interaction of the Si-H bond is least with the metal in $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HSiHPh_2$ contrary to expectations, for the more electron-rich metal is in the pentamethyl-cyclopentadienyl compound. This is due to the steric bulk of the C_5Me_5 ligand which inhibits the addition of the Si-H bond to the transition metal. In comparison to previous studies on $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiPh_3$, these studies show that the alkyl and halogen substitutions on Si have greater control than Cp ring methylation on the extent of addition of the Si-H bond to the metal center.

3. **Electronic Structure Factors of Si-H Bond Activation by Transition Metals. Effects of Ligand Substitution at the Metal Center.** D.L. Lichtenberger and A. Rai-Chaudhuri, *Inorg. Chem.*, **29**, 975 (1990).

The valence photoelectron spectra of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(L)HSiCl_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(L)HSiHPh_2$, where L is CO or $P(CH_3)_3$, have been obtained to determine the effect of ligand substitution at the metal center on Si-H bond activation. Metal centers which are more electron rich may promote more complete oxidative addition of the Si-H bond to the metal. The shifts in the metal and ligand ionization energies and the relative intensities of ionizations in the He I and He II photoelectron experiments show that the metal in $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(PMe_3)HSiCl_3$ is best represented by a formal oxidation state of III (d^4 electron count). This indicates nearly complete oxidative addition of the Si-H bond to the metal center and results in independent Mn-H and Mn-Si bonds. In contrast, the splitting and intensity pattern of the metal-based ionizations of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(PMe_3)HSiHPh_2$ reflect the formal d^6 electron count of a metal corresponding to oxidation state I. The extent of electron charge density shift from the metal to the ligand is also small as evidenced by the negligible shifts of these ionizations from those of the related $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(PMe_3)$ complex. These observations indicate that the electronic structure of the Si-H interaction with the metal in this complex is in the initial stages of Si-H bond addition to the metal, before oxidative addition has become prevalent. Comparison with the previously reported photoelectron spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$ shows that the Si-H bond interaction with the transition metal is affected more by alkyl and halogen substitutions on silicon than by substitution of a carbonyl with typical two-electron donor ligands at the metal center.

4. **Electronic Structure Factors of Ge-H Bond Activation by Transition Metals.** D.L. Lichtenberger and A. Rai-Chaudhuri, *J. Chem. Soc. Dalton Trans.*, 2161, (1990).

The He I photoelectron spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HGePh_3$, $(\eta^5\text{-}C_5H_4CH_3)\text{-}Mn(CO)_2HGePh_3$ and $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HGePh_3$ (Ph is C_6H_5) have been obtained to measure the nature and extent of Ge-H bond interaction with the transition metal center in these complexes. The principle electronic structure factors contributing to the addition of the Ge-H bond to the transition metal involve the interaction of the Ge-H σ and σ^* orbitals with the metal. The shape and splitting pattern of the metal-based ionization band indicates the extent of Ge-H σ^* interaction with the metal. The electron distribution between the Ge-H bond and the metal is indicated by the relative stabilities of the metal-based and ligand-based ionizations. The electron charge density shift from the metal to the ligand is negligible in these three complexes and the metal ionizations reflect the formal d^6 electron count at the metal center. The electronic structure of the Ge-H interaction with the metal is in the initial stages of Ge-H bond addition to the metal, before oxidative addition has become prevalent. The mechanism of interaction of the Ge-H bond with the Mn center is predominantly through interaction of the filled Ge-H σ bonding orbital with the empty metal orbitals. This result is similar to the conclusions obtained from our previous photoelectron studies on $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiPh_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$. It is concluded that the magnitude of Ge-H σ interaction with the metal center is similar to that of the Si-H σ interaction with the metal.

C. ELECTRON DONOR PROPERTIES OF MAIN GROUP MOLECULES AND METALS

1. **The Relative Electron Donor Strengths of TTF Derivatives: Effects of Chemical Substitutions and the Molecular Environment from a Combined Photoelectron and Electrochemical Study.** D.L. Lichtenberger, R.L. Johnston, K. Hinkelmann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, **112**, 3302 (1990).

Interest in organic metals and superconductors has prompted studies of the effects of chemical substituents on the organic electron donor tetrathiafulvalene (TTF). Electron donating substituents on TTF should lead to reduced ionization potentials and generally greater electron transfer in organic donor/acceptor compounds. However, the relative electron donor abilities may also be influenced by their molecular environment and intermolecular interactions. This study has provided another approach to observing the importance of the intermolecular interactions. In order to address these questions, the valence ionization potentials of TTF and two derivatives, bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), have been measured in the gas phase by photoelectron spectroscopy and compared with oxidation potentials from solution electrochemical measurements in a variety of solvents. The order of decreasing first ionization potentials is BEDT-TTF ≈ TTF (6.7 eV) > BEDO-TTF (6.46 eV). However, the order of solution oxidation potentials is BEDT-TTF > BEDO-TTF > TTF. The solvent dependence of these oxidation potentials scales linearly with the cation solvation power of the solvent, expressed as the difference between the first and second oxidation potentials of BEDO-TTF. Extrapolation to the zero-solvation limit (i.e. the gas phase) reproduces the order of ionization potentials determined by photoelectron spectroscopy. When predicting whether a derivative is a better electron donor than TTF, it is therefore necessary to consider the molecular environment of the donor molecule. The nature of solvation and/or interaction with the acceptor molecules may result in trends which are opposite to those based purely on ionization potentials or theoretical calculations on single isolated molecules.

2. **Electronic Structure and Bonding in Four-coordinate Organometallic Complexes of Aluminum.** D.L. Lichtenberger, R.H. Hogan, M.D. Healy and A.R. Barron, *J. Am. Chem. Soc.*, **112**, 3369 (1990).

The He I valence photoelectron spectra of the Lewis acid-base adducts $Me_3Al(PMe_3)$ and $Me_2(BHT)Al(PMe_3)$ (BHT-H = 2,6-di-tert-butyl-4-methyl-phenol) have been obtained to characterize the electronic structure and bonding in four-coordinate organometallic complexes of aluminum. This is our first comparison of the bonding of small molecules to transition metals and to main group metals. To aid in the assignment of the spectrum of $Me_2(BHT)Al(PMe_3)$, the spectrum of the free alcohol, BHT-H, was also obtained. The first and second ionizations of the free BHT-H alcohol show vibrational progressions associated with the symmetric C-C phenyl ring stretching modes, consistent with the b_1 and a_2 π ionizations, respectively, of monosubstituted phenyl rings. In the photoelectron spectrum of BHT coordinated to aluminum in $Me_2(BHT)Al(PMe_3)$, the corresponding phenoxide a_2 ionization retains the vibrational structure, but the individual vibrational components are lost in the ionization which corresponds most closely with the b_1. The loss of vibrational fine structure associated with ionization from the phenyl π b_1 orbital in the coordinated phenoxide shows that the phenoxide is involved in a π interaction with the $Me_2Al(Me_3)$ portion of the molecule. In addition, the aluminum center in $Me_2(BHT)Al(PMe_3)$ feels a more negative charge potential than the aluminum center in $Me_3Al(PMe_3)$, as shown by the Al-P σ ionization occurring at lower binding energy in $Me_2(BHT)Al(PMe_3)$. This is counter to the σ inductive effects of an alkoxide compared to an alkyl and shows that the BHT is acting as a π electron donor. The change in bandshape of the Al-P σ ionization between $Me_3Al(PMe_3)$ and $Me_2(BHT)Al(PMe_3)$ indicates that the oxygen pπ orbital of the phenoxide ligand is interacting directly with the Al-P bonding orbital. The relationship between experimental ionization potentials and bond strengths of the Al-P σ bond in $Me_3Al(PMe_3)$ and $Me_2(BHT)Al(PMe_3)$ has been developed, and the results show that the Al-P σ bond is stronger in $Me_3Al(PMe_3)$ than in $Me_2(BHT)Al(PMe_3)$, consistent with π donation from the phenoxide into the predominantly Al-P σ^* orbital.

3. **Electronic Structure and Bonding in Four-Coordinate Organometallic Complexes of Aluminum. The Effects of Pyridine Substitution.** D.L. Lichtenberger, R.H. Hogan, M.D. Healy and A.R. Barron, *Organometallics*, **10**, 609-614 (1991).

The He I valence photoelectron spectra of the Lewis acid-base adducts, $Me_3Al(py)$ and $Me_2(BHT)Al(py)$ (BHT = 2,6-di-tert-butyl-4-methyl phenoxide, py = pyridine, Me = methyl) have been obtained in order to further characterize the electronic structure and bonding in four-coordinate organometallic complexes of aluminum. In the photoelectron spectrum of the BHT ligand coordinated to aluminum in $Me_2(BHT)Al(py)$, the phenyl π a_2 ionization of the phenoxide ligand (Phπ a_2) retains the vibrational structure observed in the free alcohol (BHT-H), but the individual vibrational components are lost in the ionization which corresponds most closely with the Phπ b_1. The loss of vibrational fine structure associated with ionization from the Phπ b_1 orbital in the coordinated phenoxide shows that the phenoxide is involved in a π interaction with the $Me_2Al(py)$ portion of the molecule. The similarity of the splits of the Phπ a_2 and b_1 ionizations in $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$ shows that the extent of the π interaction of the BHT ligand with the $Me_2Al(PMe_3)$ and $Me_2Al(py)$ portions of the molecules is about the same. The Phπ a_2 and b_1 ionizations of the BHT ligand experience a destabilizing shift on proceeding from $Me_2(BHT)Al(py)$ to $Me_2(BHT)Al(PMe_3)$. This increase in negative charge potential at the metal center when the trialkylphosphine replaces the pyridine follows from the expected better σ donor ability of the trialkylphosphine and the potentially better π acceptor ability of the pyridine ligand. The pyridine ionizations show several interesting trends. First, the pyridine π ionizations in $Me_3Al(py)$ are destabilized in comparison to the same ionizations of free pyridine, showing that the pyridine experiences a net negative charge potential when it is coordinated to Me_3Al. Since the aluminum is in its highest formal oxidation state, the net negative charge potential must involve the Al-Me σ bonds and/or π donation from the methyl C-H σ bonds. Second, on proceeding from $Me_3Al(py)$ to $Me_2(BHT)Al(py)$, the pyridine π ionizations show the expected stabilization from the more positive potential at the aluminum center that results from replacing a methyl group with the more electronegative alkoxide. However, the coordinated nitrogen lone-pair ionization shows a destabilization, as also observed in the study of the analogous phosphine complexes. This destabilization again traces to overlap interaction with the π donor orbital of the alkoxide. These results suggest that π symmetry interactions with ligands from the first row of the periodic table may be a prevalent aspect of the chemistry of four-coordinate aluminum complexes.

III. INSTRUMENTATION AND METHODS DEVELOPMENT

As discussed in the proposals and previous progress reports, the continuing improvement in our experimental and computational capabilities for investigating these properties is an important aspect of this program. Several upgrades have been made on our existing gas phase photoelectron spectrometer, and progress continues on the new second spectrometer. The prospects for experiments on the new spectrometer are particularly exciting. Our theoretical and modeling capabilities are also continuing to move forward. The acquisition of new programs and the modification and development of current software allows us to fully utilize the enhanced capabilities of our new computers and workstations in this department.

A. Gas Phase Photoelectron Spectroscopy Development

Two separate gas phase photoelectron spectrometers are being developed. The first spectrometer has been used to collect the data described in this report. It is being upgraded as described below. The second spectrometer has been dedicated to developing the instrumentation for gas phase photoelectron spectroscopy. The sample chamber of the second spectrometer has been completely redesigned to allow combined UPS, XPS, and Auger capabilities.

In the previous period, a newly designed differential pumping chamber for the He I/He II lamps had been constructed for the first spectrometer. The efficiency of He I or He II photon sources for ionization depends greatly upon the removal of excess He escaping from the lamp. In the most recent period we have also completely redesigned the He II photon source. The new design is the result of numerous experiments and modifications for trapping the discharge in the correct region of the source and obtaining the highest and most stable flux of photons. After optimization of this source, we found that under the correct conditions of He pressure and voltage (with a change in polarity), the source also produces a high flux of He I photons. This is extremely fortunate, because it is now no longer necessary to remove one source and bolt on the other for He I and He II experiments.

The desire to obtain a high-quality gas-phase photoelectron spectrum of buckminsterfullerene inspired us to improve the high-temperature capabilities of our instrumentation. C_{60} sublimes at temperatures near 400°C, and the higher fullerenes and derivatives are anticipated to sublime at higher temperatures. In our previous instrumentation, many of the aluminum components would also sublime at these temperatures. These aluminum components have now been replaced with higher temperature materials. Interestingly, these improvements have opened the door to study a number of other interesting high-temperature species in the next period of this program.

The new XPS and Auger sources for the combined UPS, XPS, Auger gas phase spectrometer were completed in the previous period. The sample chamber for incorporating these sources was also completed and the chamber was constructed in the most recent period. The improvement in sensitivity from this instrument and the ability to investigate chemical systems that were previously not possible indicates that the next period of the program should be particularly exciting.

B. Thin Film Surface Photoelectron Spectroscopy and Scanning Tunneling Microscopy Development.

During the last year we have continued to refine our techniques for the deposition of organometallic complexes on surfaces. We have added a second effusion cell to our deposition chamber which increases the sample throughput in our experiments. We have also added a quartz crystal microbalance and a quadrupole mass spectrometer to more precisely monitor the deposition process, as we indicated we would in last year's progress report. Development of abilities to deposit a whole range of compounds will continue, including deposition of a range of materials from highly volatile compounds requiring low temperature stages to metals at high temperature and voltages.

Some of the most exciting accomplishments in our studies of thin films have been the breakthroughs with scanning tunneling microscopy. These studies have been carried out in collaboration with Professor Dror Sarid in the Department of Optical Sciences at the University of Arizona. We are now developing the instrumentation for the study of air-sensitive samples under nitrogen and for the study of thin films in ultra-high vacuum. Initial experiments in both areas have been successful.

C. Analytical Modeling of Valence Ionizations. D.L. Lichtenberger and A.S. Copenhaver, *J. Elec. Spec. Rel. Phen.*, **50**, 335 (1990).

As the field of valence photoelectron spectroscopy matures it is important that valence ionizations be reported more precisely and consistently in the literature. Other areas of spectroscopy have included extensive studies of band deconvolution and fitting procedures for extracting chemically useful information from the methods. We have investigated models of ionization band profiles on both a theoretical and a practical basis and found that a particular asymmetric band model conveniently represents the unresolved photoelectron ionization band. Methods for evaluation of a photoelectron spectral fit and determination of the goodness of fit have been developed. The publication of these results has been submitted in this period of the project, and the computer programs are being made generally available.

In the publication, the analytical descriptions of partially resolved and unresolved vibrational progressions in valence photoelectron ionization bands are discussed. The ${}^2T_{2g}$ valence ionization of $Cr(CO)_6$ is examined as an example of a partially resolved vibrational progression, and the Jahn-Teller split ${}^2E'$ and ${}^2E''$ valence ionizations of $Fe(CO)_5$ are examined as examples of overlapping ionizations with unresolved vibrational progressions. Asymmetric Gaussian band shapes are obtained when vibrational broadening is responsible for the overall contour of the molecular ionization. Attempts to model the valence ionizations with symmetric Gaussian peak models can lead to serious misrepresentations of the ionization bands. This is found to be particularly important for overlapping ionizations such as the Jahn-Teller split bands of $Fe(CO)_5$, where attempts to model the contours with symmetric Gaussian peak shapes leads to physically unreasonable band positions, relative amplitudes, halfwidths and band areas. The treatment of ionizations with resolved vibrational fine structure is also addressed for the $^2A_{1g}$ ionization of osmocene. A series of related Gaussian components are used to model the resolved vibrational progressions. The goodness of fit between the model and the data is discussed in each case and a method for determining the statistical confidence of additional parameters in the fit is examined. Advantages and limitations in the analytical representation of valence photoelectron data are addressed.

D. Theory and Molecular Modeling Developments.

We have continued to develop our methods for theoretical calculations of the electronic structure of transition metal complexes. A new version of the Fenske-Hall approximate molecular orbital program has been acquired and installed. This program has now become the standard for initial theoretical calculations on these systems. A major accomplishment during this period has been the award from NSF to acquire a departmental minisupercomputer. I was the principle writer on this proposal. We acquired a Convex 220 minisupercomputer with this funding. This computer is greatly increasing the sophistication of the theoretical calculations used in these investigations.

We have also initiated a molecular modeling study of the scanning tunneling microscopy experiment. Initial modeling has been carried out on a Silicon Graphics Iris workstation. A program SURFER has been written which simulates the image obtained when the STM tip scans over a molecule or a group of molecules. At present, the program assumes a rigid atom model. More sophisticated modeling is planned in the coming period.

IV. PUBLICATIONS DURING CURRENT PERIOD OF DE-FG02-86ER13501

The sources of funding for each publication are listed in parentheses at the end of each reference. In each case the primary source of funding is listed first. The other agencies contribute only indirectly in the sense that they also support the instrumentation and facilities used by all projects, and this is acknowledged in the publications. The individual agencies and the projects they support are summarized in Section VII.

A. Appeared

1. D.L. Lichtenberger, G.P. Darsey, G.E. Kellogg, R.D. Sanner, V.G. Young and J.R. Clark, "Relative Strengths of Early Transition Metal M-H and M-C Bonds in Substituted Niobocenes and Tantalocenes. Thermodynamic Trends and Electronic Factors of Olefin Insertion Into a Metal-Hydride Bond," *J. Am. Chem. Soc.*, **111**, 5019 (1989). (DOE, MCP)

2. D.L. Lichtenberger, A. Rai-Chaudhuri, "Electronic Structure Factors of Si-H Bond Activation by Transition Metals. The Valence Photoelectron Spectrum of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$," *J. Am. Chem. Soc.*, **111**, 3583-3591, (1989). (Operating costs, DOE; A.R-C. salary, PRF/DOE)

3. D.L. Lichtenberger and A.S. Copenhaver, "Experimental Measures of the Electron Distribution and Bonding in bis(η^5-Cyclopentadienyl)Osmium from He(I) and He(II) Valence Photoelectron Spectroscopy," *J. Chem. Phys.*, **91**, 663-673 (1989). (DOE)

4. D.L. Lichtenberger and R.L. Johnston, "Experimental Measures of Metal-Metal Sigma, Pi, and Delta Bonding from Photoelectron Spectroscopy," *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*, J.P. Fackler, Jr., Ed. Plenum, (1990). (NSF)

5. D.L. Lichtenberger and A. Rai-Chaudhuri, "Electronic Structure Control of Si-H Bond Activation by Transition Metals. The Valence Photoelectron Spectra of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiPh_3$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiFPh_2$ (Ph = C_6H_5)," *J. Am. Chem. Soc.*, **112**, 2492 (1990). (Operating costs, DOE; A.R-C. salary, PRF/DOE)

6. D.L. Lichtenberger and A. Rai-Chaudhuri, "Electronic Structure Factors of Si-H Bond Activation by Transition Metals. The Valence Photoelectron Spectra of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(PMe_3)HSiCl_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)(PMe_3)HSiHPh_2$ (Me is CH_3, Ph is C_6H_5)", *Inorg. Chem.*, **29**, 975 (1990). (Operating costs, DOE; A.R-C. salary, PRF/DOE)

7. D.L. Lichtenberger, R.L. Johnston, K. Hinkelmann, T. Suzuki and F. Wudl, "The Relative Electron Donor Strengths of TTF Derivatives: Effects of Chemical Substitutions and the Molecular Environment from a Combined Photoelectron and Electrochemical Study," *J. Am. Chem. Soc.*, **112**, 3302 (1990). (DOE)

8. D.L. Lichtenberger and A.S. Copenhaver, "Ionization Band Profile Analysis in Valence Photoelectron Spectroscopy," *J. Elec. Spec. Rel. Phen.*, **50**, 335 (1990). (NSF, DOE)

9. D.L. Lichtenberger, R.H. Hogan, M.D. Healy and A.R. Barron, "Electronic Structure and Bonding in Four-Coordinate Organometallic Complexes of Aluminum. The Valence Photoelectron Spectra of BHT-H, $Me_3Al(PMe_3)$ and $Me_2(BHT)Al(PMe_3)$ (BHT=2,6-di-tert-butyl-4-methylphenoxide)," *J. Am. Chem. Soc.*, **112**, 3369 (1990). (DOE; R.H.H. salary, NSF/DOE)

10. D.L. Lichtenberger and A.S. Copenhaver, "Ionization Energy-Bond Energy Relationships in Organometallic Chemistry," in *Bonding Energetics in Organometallic Compounds*, Marks, Tobin J., Ed., A.C.S. Symposium Series, 428 (1990). (DOE)

11. D.L. Lichtenberger, A.S. Copenhaver and J.L. Hubbard, "The Electronic Structure of Nitrosyl and Carbonyl Supported Metal-Metal Interactions. The Photoelectron Spectra of $[\eta^5\text{-}(C_5H_5)Fe(\mu\text{-}NO)]_2$, $[\eta^5\text{-}(C_5(CH_3)_5)Fe(\mu\text{-}NO)]_2$, $[\eta^5\text{-}(C_5H_5)Ru(\mu\text{-}NO)]_2$ and $[\eta^5\text{-}(C_5(CH_3)_5)Co(\mu\text{-}CO)]_2$," *Polyhedron* Vol. 9, No. 15/16, 1783-1797 (1990). (NSF, DOE)

12. C.S.J. Chang, A. Rai-Chaudhuri, D.L. Lichtenberger, and J.H. Enemark, "He I Valence Photoelectron Spectra of Oxomolybdenum(V) Complexes Containing Diolato or Alkoxide Ligands," *Polyhedron*, Vol. 9, No. 15/16, 1965-1973 (1990). (NSF, MCP)

13. D.L. Lichtenberger and A. Rai-Chaudhuri, "Cyclopentadienyl Ring Methylation and Its Effect on Si-H Bond Activation in $(\eta^5\text{-}C_5H_{5-n}(CH_3)_n)Mn(CO)_2HSiH(C_6H_5)_2$ (n = 0,1,5) Complexes," *Organometallics*, **9**, 1686 (1990). (Operating costs, DOE; A.R-C. salary, PRF/DOE)

14. D.L. Lichtenberger and A. Rai-Chaudhuri, "Electronic Structure Factors of Ge-H Bond Activation by Transition Metals. Photoelectron Spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HGePh_3$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HGePh_3$ and $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HGePh_3$ (Ph is C_6H_5)," *J. Chem. Soc.* Dalton Trans., 2161 (1990). (Operating costs, DOE; A.R-C. salary, PRF/DOE)

15. D.L. Lichtenberger, S.K. Renshaw, F. Basolo and M. Cheong, "The Photoelectron Spectroscopy and Rates of CO Substitution of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ Compounds. Separation of σ and π Ring Substituent Effects," *Organometallics*, **10**, 148-156 (1991). (DOE, NSF, MCP)

16. D.L. Lichtenberger, R.H. Hogan, M.D. Healy and A.R. Barron, "Electronic Structure and Bonding in Four-Coordinate Organometallic Complexes of Aluminum. The Valence Photoelectron Spectra of $(CH_3)_3Al$(pyridine) and $(CH_3)_2$(BHT)Al(pyridine) (BHT=2,6-Di-tert-butyl-4-methylphenoxide)," *Organometallics*, **10**, 609-614 (1991). (DOE, NSF, MCP)

17. D.L. Lichtenberger and A. Rai-Chaudhuri, "The Electronic Structure of Transition Metal-Silicon Bonds. The Valence Photoelectron Spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2L$ Complexes (L = $SiCl_3$, $Si(CH_3)_3$)," *J. Am. Chem. Soc.*, **113**, 2923-2930 (1991). (PRF, DOE, NSF, MCP)

18. D.L. Lichtenberger, A. Rai-Chaudhuri, M.J. Seidel, J.A. Gladysz, S.K. Agbossou, A. Igau and C.H. Winter, "Delocalized Electronic Interactions in Chiral Cyclopentadienyl Rhenium Halide Complexes. The Valence Photoelectron Spectra of CpRe(NO)(L)X (Cp is $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5(CH_3)_5$, L is CO and $P(C_6H_5)_3$, X is Cl, Br, and I)," *Organometallics*, **10**, 1355-1364 (1991). (A.R-C. salary, PRF/DOE, NSF)

19. D.L. Lichtenberger, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb, "Valence and Core Photoelectron Spectroscopy of C_{60}, Buckminsterfullerene," *Chem. Phys. Lett.*, **176**, 203-208 (1991). (DOE, NSF, MCP)

20. D.L. Lichtenberger, M.E. Jatcko, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb, "The Ionizations of C_{60} in the Gas Phase and in Thin Solid Films," *Mat. Res. Soc. Symp. Proc*, **206** 673-678 (1991). (DOE, NSF, MCP)

21. T. Chen, S. Howells, M. Gallagher, L. Yi, D. Sarid, D.L. Lichtenberger, K.W. Nebesny and C.D. Ray, "Modelling of the Intramolecular Structure of Monolayer C_{60} Molecules Observed with Scanning Tunneling Microscopy," *Mat. Res. Soc. Symp. Proc*, **206** 721-725 (1991). (DOE, NSF, MCP)

B. Currently in Press

22. D.L. Lichtenberger, A. Rai-Chaudhuri, and R.H. Hogan, "Experimental Comparison of the Bonding in Inorganometallic and Organometallic Complexes by Photoelectron Spectroscopy," *Inorg. Chem.*, T.P. Fehlner, Ed., Plenum, accepted. (NSF, DOE)

23. D.L. Lichtenberger and M.E. Jatcko, "Electronic Structure of Monodentate Coordinated Diphosphine Complexes. The Photoelectron Spectra of $Mo(CO)_5(P(CH_3)_2CH_2P(CH_3)_2)$ and $Mo(CO)_5(P(CH_3)_2CH_2CH_2P(CH_3)_2)$," *Inorg. Chem.*, accepted. (DOE)

24. T. Chen, S. Howells, M. Gallagher, L. Yi, D. Sarid, D.L. Lichtenberger, K.W. Nebesny and C.D. Ray, "Internal Structure and Two-Dimensional Order of Monolayer C_{60} Molecules on Gold Substrate," *J. Vac. Sci. & Tech.*, accepted. (DOE)

C. Submitted

25. D. Sarid, T. Chen, S. Howells, M. Gallagher, L. Yi, D.L. Lichtenberger, K.W. Nebesney and C.D. Ray, "Atomic Force Microscopy of C_{60} Molecules on a Gold Substrate," *Applied Phys. Lett.*, submitted 7/91. (DOE)

26. S. Howells, T. Chen, M. Gallagher, D. Sarid, D.L. Lichtenberger, L.L. Wright, C.D. Ray, D.R. Huffman and L.D. Lamb, "High Resolution Images of Single C_{60} Molecules on Gold (111) Using Scanning Tunneling Microscopy," *Science*, submitted 9/91. (DOE/NSF)

Note: Numerous other manuscripts are in preparation. Publication of results will continue at the present or greater rate.

D. Ph.D. Dissertations

27. "Photoelectron Spectroscopy of Supported Metal-Metal Interactions," Ann Savena Copenhaver, University of Arizona, 1989 (*Diss. Abstr. Int. B* **1990**, 50(8), 3464).

28. "Electronic Structure and Bond Energy Trends in Si-H and Ge-H Bond Activation by Transition Metals," Anjana Rai-Chaudhuri, University of Arizona, 1989 (*Diss. Abstr. Int. B* **1989**, 50(5) 1932).

29. "Scanning Tunneling Microscopy and Photoelectron Spectroscopy of This Film Dichromium Tetraacetate and Dimolybdenum Tetraacetate on Single Crystal Graphite and Molybdenum Disulphide," Royston Hugh Hogan, University of Arizona, 1990 (*Diss. Abstr. Int. B* **1990**, 51(4), 1813).

30. "Effect of Ligand Addition and Substitution on Metal-Metal Multiple Bonds: Direct Electronic Structure Comparisons via Gas-Phase Photoelectron Spectroscopy," Garry Dale Hinch, University of Arizona, 1990 (*Diss. Abstr. Int. B* **1990**, 51(8), 3835).

31. "Ionization-Structure Relationships in Metal-Phosphine Interactions," Mark Edward Jatcko, University of Arizona, 1990 (*Diss. Abstr. Int. B* **1990**, 51(1), 200).

32. "Photoelectron Spectroscopy and Bonding of Iron and Rhodium Organometallic Compounds with Metal-Carbon and Metal-Hydrogen Bonds," Sharton Kintner Renshaw, University of Arizona, 1991.

V. PRESENTATIONS

A. Invited

1. Texas A&M, IUCCP Symposium on Metal-Metal Bonds and Clusters in Chemistry and Catalysis, March 1989.

2. Symposium for 1989 ACS Award in Inorganic Chemistry, 197th National Meeting of the American Chemical Society Meeting, Dallas, April 1989.

3. Inorganic Chemistry Division Symposium, 198th National Meeting of the American Chemical Society, Miami, September, 1989.
4. "Ionization Energy - Bond Energy Relationships in Organometallic Chemistry," Dennis L. Lichtenberger and Ann S. Copenhaver, 198th National ACS Meeting, Miami, Florida, September 10-15, 1989.
5. University of Pittsburgh, January, 1990.
6. Materials Characterization Program, University of Arizona, March, 1990.
7. NSF Organometallic Workshop, Lexington, Kentucky, May, 1990.
8. Inorganic Division of the Canadian Society for Chemistry, Halifax, Nova Scotia, Canada, July, 1990.
9. Inorganometallic Symposium, 200th National Meeting of the American Chemical Society, Washington, D.C., August, 1990.
10. University of Illinois, October, 1990.
11. Jack T. Spence Lecture Series, Utah State University, November, 1990.
12. Materials Research Society Symposium, Boston, MA, November 1990.
13. Ninth Biennial Carl S. Marvel Symposium, University of Arizona, Tucson, March 1991.
14. Garvan Symposium, 201st National Meeting of the American Chemical Society, Atlanta, GA, April 1991.
15. Gordon Research Conference on Organometallic Chemistry, Salve Regina College, Newport, RI, July 1991.
16. University of Texas, El Paso, September 1991.

B. Contributed

17. "Scanning Tunneling Microscopy and Photoelectron Spectroscopy of $Mo_2(O_2CCH_3)_4$ Deposited on Single Crystal Graphite," Royston H. Hogan and Dennis L. Lichtenberger, 1989 Gordon Organometallic Conference, July 17-21, 1989.
18. "Electronic Structure Trends in $(\eta^5\text{-}C_5H_5)Re(CO)(NO)X$ and $[\eta^5\text{-}(CH_3)_5C_5]Re(CO)(NO)X$ Compounds by Photoelectron Spectroscopy. X = F, Cl, Br, I," Anjana Rai-Chaudhuri, Matthew J. Seidel and Dennis L. Lichtenberger, 1989 Gordon Organometallic Conference, July 17-21, 1989.
19. "Electronic Structure Control of Si-H Bond Activation by Transition Metals," Anjana Rai-Chaudhuri and Dennis L. Lichtenberger, 198th National ACS Meeting, Miami, Florida, September 10-15, 1989.
20. "Scanning Tunneling Microscopy and Photoelectron Spectroscopy of $Mo_2(O_2CCH_3)_4$ Deposited on Single Crystal Graphite," Royston H. Hogan, Dennis L. Lichtenberger, Y.C. Lee, D. Sarid, M.A. Bruck, R.L. Johnston, K.W. Nebesny, M. Vallarba, N. Nunes, 1989 Pacific Conference on Chemistry and Spectroscopy, October 18-21, 1989.
21. "Scanning Tunneling Microscopy and Photoelectron Spectroscopy of $Mo_2(O_2CCH_3)_4$ Deposited on Single Crystal Graphite," Y.C. Lee, D. Sarid, D.L. Lichtenberger, M.A. Bruck, R.H. Hogan, R.L. Johnston and K.W. Nebesny; Gordon Organometallic Conference, Newport, RI, 1989.

22. "Electronic Structure Trends in (η^5-C_5H_5)Re(CO)NO)X and [η^5-$(CH_3)_5C_5$]Re(CO)(NO)X Compounds by Photoelectron Spectroscopy. X = F, Cl, Br, I," A. Rai-Chaudhuri, M.J. Seidel, D.L. Lichtenberger and J.A. Gladysz; Gordon Organometallic Conference, Newport, RI, 1989.

23. "Scanning Tunneling Microscopy and Photoelectron Spectroscopy of Thin Film $Cr_2(O_2CCH_3)_4$ and $Mo_2(O_2CCH_3)_4$ on Single Crystal Graphite and MoS_2," R.H. Hogan and D.L. Lichtenberger; 199th ACS National Meeting, Boston, MA, 1990.

24. "Ionization Energies and Chemistry," D.L. Lichtenberger; 199th ACS National Meeting, Boston, MA, 1990.

25. "Photoelectron Spectra and Electronic Structure of Organometallic Rhenium Halide Complexes, the First Photoelectron Spectrum of a Metal Fluoride Complex," A. Rai-Chaudhuri and D.L. Lichtenberger; 199th ACS National Meeting, Boston, MA, 1990.

26. "Ionization-Structure-Reactivity Relationships in Transition Metal Chemistry," D.L. Lichtenberger; 14th NSF Workshop in Organometallic Chemistry, Lexington, KY, 1990.

27. "The Electronic Structure Effects of Coordination Geometry Differences in Metal Carbonyl Complexes Containing Monodentate Phosphines Versus a Chelating Diphosphine Analogue. Electronic and Steric Balance in Metal-Phosphine Coordination via the *Phosphine Twist*," D.L. Lichtenberger and M.E. Jatcko; Inorganic Division of the Canadian Society for Chemistry, Halifax, Nova Scotia, Canada, 1990.

28. "Experimental Characterization of the Electronic Structure and Bonding in Inorganometallic Complexes by Gas Phase Photoelectron Spectroscopy," D.L. Lichtenberger, A. Rai-Chaudhuri and R.H. Hogan; 200th National ACS Meeting, Washington, D.C., 1990.

29. "The Ionizations of C_{60} in the Gas Phase and in Thin Solid Films," D.L. Lichtenberger, M.E. Jatcko, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb, Materials Research Society Symposium, Late News Sessions, November 1990.

30. "Intramolecular Structure and Two-dimensional Order of Monolayer C_{60} on Gold Substrate," T. Chen, S. Howells, M. Gallagher, L. Yi, D. Sarid, D.L. Lichtenberger, K.W. Nebesny and C.D. Ray; 1991 Meeting of the American Physical Society, March 1991.

31. "The Photoelectron Spectroscopy of C_{60}, Buckminsterfullerene, in the Gas Phase and on Surfaces. Relationships with Images in Scanning Tunneling Microscopy. D.L. Lichtenberger, M.E. Jatcko, K.W. Nebesny, C.D. Ray, D.R. Huffman and L.D. Lamb; 201st National ACS Meeting, Atlanta, Georgia, April 1991.

32. "Principles and Examples of Scanning Force Microscopy," D. Sarid, T. Chen, L. Yi, S. Howells, M. Gallagher and D. Lichtenberger; 202nd National ACS Meeting, New York City, NY, August 1991.

VI. PERSONNEL

A. Postdoctoral Associates, Graduate Students, Undergraduates, Visiting Faculty, and Staff

1. Ann S. Copenhaver, DOE research associate, 7/1/86-5/30/89, postdoctoral research associate, 6/1/89-12/30/89, theoretical principles of ionization energy-bond energy relationships, bonding in osmocene, metal-metal and metal-methylene bonds, analytical models of valence ionizations.

2. Mark E. Jatcko, NSF research associate, 2/87-12/89; postdoctoral research associate, 1/90-5/91 (support matched by MCP), new instrument development for gas phase photoelectron spectroscopy, additive ligand electronic effects, metal-phosphine complexes.
3. Anjana Rai-Chaudhuri, PRF/DOE postdoctoral research associate, 7/1/87-9/25/90, activation of silicon-hydrogen bonds.
4. Royston H. Hogan, NSF/DOE research associate, 6/13/88-5/30/90, postdoctoral research associate, 6/1/90-9/25/90, metal-metal bonds.
5. Sharon K. Renshaw, DOE research associate, 1/15/87-present, reactivity of late-metal cyclopentadienyl complexes, ionization energy relationships with Hammet σ parameters, oxidative C-H bond additions, Ph.D. October 1991, bonding of acetylides in organometallics.
6. Roy L. Johnston, NATO postdoctoral fellow, 10/3/88-8/31/89, metal-sulfur interactions and metal-metal bonds.
7. Dr. Laura Wright, Associate Professor, Furman University, NSF Research Opportunity Award visiting researcher, 6/24/91-present, STM of organic molecules on metals.
8. Lalitha Subramanian, NSF postdoctoral research associate, 8/27/91-present, early transition metal-metal bonds.
9. Nadine Gruhn, NSF research associate, 1/1/90-present, metal-silicon bonds.
10. Mara Rempe, DOE research associate, 1/1/90-present, electronic structure of fullerenes.
11. Charles Ray, NSF research associate, 1/1/90-present, surface studies of metal-metal bonds.
12. Matthew Seidel, DOE/NSF undergraduate assistant, 5/11/89-present, construction of a new photoelectron spectrometer.
13. Stefan Gogosha, volunteer undergraduate assistant, 2/91-present, preparation of buckminsterfullerene.
14. Marie Villarba, Research Experiences for Undergraduates program, summer 1989, theoretical modeling of STM.
15. Nici Nunes, Research Experiences for Undergraduates program, summer 1989, STM of photohalocyanines.
16. Damaris Chong, undergraduate assistant, 1989, synthesis of organometallic molecules.
17. Kim Schwink, Research Experiences for Undergraduates program, summer 1990, ionization-proton affinity relationships.
18. Thu-Mai Duong, undergraduate assistant, 1990, preparation of CpMn(CO)$_2$L complexes.
19. Amy Bjerke, Research Experiences for Undergraduates program, summer 1991, photoelectron spectroscopy of nitrogen heterocycles and porphyrins.
20. Melanie Nilsson, Research Experiences for Undergraduates program, summer 1991, preparation of derivatives of buckminsterfullerenes.
21. Dona Myers, full time secretary serving this research group and the Enemark research group. Supported one-sixth by DOE funding, one-sixth by NSF, and matched one-third by Professor Enemark and one-third by the Department.

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