**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) accomplished the high-resolution gas phase photoelectron spectra of C_{60} and C_{70} , (2) characterized the electronic features of imaging C_{60} on gold by STM, (3) evaluated the orbital distributions of C_{60} and the bonding interactions with metals, (4) revealed details of the bonding of phosphines to metals, including the subtleties of a geometrical twist in sterically crowded situations, (5) determined the formal electron distribution in the bonding of η^3 -cyclopropenyl with metals, (6) related gas-phase ionization energies to electron transfer kinetics and ion solvation thermochemistry of metallocenes, (7) correlated lone-pair ionization energies with proton affinities for a variety of amino acids and related compounds, (8) examined sigma-pi interactions in non-conjugated polyalkynes, (9) characterized extensive metal-ligand π interactions in metal-acetylide compounds, and (10) continued to develop the experimental and theoretical methods for these studies. All of these studies have contributed significantly to expanding our understanding of the electronic structure and bonding of organic molecules and the ways this electronic structure is altered by interaction with metals. 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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**CHEMICAL ACTIVATION OF MOLECULES BY METALS:
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I. INTRODUCTION

The research in this project has continued to be successful and rewarding during the present funding period. One indication of the increasing breadth of the program is the variety of major journals in several different fields, in which our work has appeared. This has greatly expanded the audience of our investigations. The journals include the *Journal of the American Chemical Society* (3), *Inorganic Chemistry*, *Journal of Vacuum Science and Technology*, *Ultramicroscopy*, *Surface Science*, *Chemical Physics Letters*, *Synthetic Metals*, *Organometallics* (3), *International Journal of Mass Spectrometry and Ion Processes*, *Journal of Coordination Chemistry*, *Journal of the Chemical Society*, *Perkin Transactions*, *Journal of Organometallic Chemistry*, and the *Journal of Chemical Physics*. The number of publications and presentations of new work has remained at a high level, as shown in Section II. This productivity is likely to increase, as evidenced by the number of manuscripts that are near completion, the progress in the projects presently underway, the progress in construction of our second and much improved instrument for gas phase photoelectron spectroscopy, and the increased commitment of the Department of Chemistry and the University of Arizona to this Laboratory for Photoelectron Spectroscopy. On this latter point, the University has established an academic professional staff position devoted to gas phase photoelectron spectroscopy. This position will assist this research program and the numerous collaborative projects of this laboratory with others across the country. The search for a Ph.D. level person for this position is presently underway, and we have several outstanding candidates. There are also several new students, postdoctorals, and visiting faculty who are contributing to this research (Section V).

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. One development that could not be anticipated at the time of writing the previous proposal was the discovery of methods to prepare the fullerenes in quantities that allow detailed characterization of their properties. In addition to the ideal nature of our experimental methods for studying the electronic structure of the fullerenes themselves, these systems also lent themselves to the central theme of this project, which is to understand the electronic interactions of organic molecules with metals. The C_{60} molecule has unique properties that follow from its geometric and electronic structure which were able to give us new insights into these interactions. Our first paper in this area turned out to be the *thirteenth* most cited paper of 1991 and was a feature of *The Scientist*. This

alone called our work to the attention of numerous other scientists throughout the world and has led to many enlightening interactions with scientists in other fields.

This report collects some of the accomplishments of this research program during the most recent period of this project. Abstracts 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. One consequence of the considerable success with the studies of the fullerenes is that some of the other projects in the previous proposal were given less attention. We will continue to study the fullerenes where our approaches are unique and where the studies fit into the scope of this project, but we intend in the next period to emphasize going back to the previous projects that originally resulted in funding for this program.

II. PUBLICATIONS DURING CURRENT PERIOD OF DE-FG02-86ER13501, 1991-1994

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. Titles and Abstracts of Publications from this Funding Period

1. **The Photoelectron Spectroscopy and Rates of CO Substitution of $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})_2$ Compounds. Separation of σ and π Ring Substituent Effects.** D.L. Lichtenberger, S.K. Renshaw, F. Basolo and M. Cheong, *Organometallics*, **10**, 148-156 (1991). (DOE)

The He I photoelectron spectra for a series of monosubstituted $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})_2$ compounds have been obtained (where $\text{X} = \text{NO}_2$, CF_3 , Cl , H , CH_3 , or $\text{N}(\text{CH}_3)_2$). 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 $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})_2$ 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 -C₅H₄X)Rh(CO)₂PPh₃ is stabilized through π delocalization on the Cp ring.

2. Electronic Structure and Bonding in Four-Coordinate Organometallic Complexes of Aluminum. The Valence Photoelectron Spectra of (CH₃)₃Al(pyridine) and (CH₃)₂(BHT)Al(pyridine) (BHT=2,6-Di-tert-butyl-4-methylphenoxide). D.L. Lichtenberger, R.H. Hogan, M.D. Healy and A.R. Barron, *Organometallics*, **10, 609-614 (1991). (DOE)**

The He I valence photoelectron spectra of the Lewis acid-base adducts, Me₃Al(py) and Me₂(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 Me₂(BHT)Al(py), the phenyl π a₂ ionization of the phenoxide ligand (Ph π a₂) 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 Ph π b₁. The loss of vibrational fine structure associated with ionization from the Ph π b₁ orbital in the coordinated phenoxide shows that the phenoxide is involved in a π interaction with the Me₂Al(py) portion of the molecule. The similarity of the splits of the Ph π a₂ and b₁ ionizations in Me₂(BHT)Al(PMe₃) and Me₂(BHT)Al(py) shows that the extent of the π interaction of the BHT ligand with the Me₂Al(PMe₃) and Me₂Al(py) portions of the molecules is about the same. The Ph π a₂ and b₁ ionizations of the BHT ligand experience a destabilizing shift on proceeding from Me₂(BHT)Al(py) to Me₂(BHT)Al(PMe₃). 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 Me₃Al(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 Me₃Al. 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 Me₃Al(py) to Me₂(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.

3. Electronic Structure of Transition Metal-Silicon Bonds. The Valence Photoelectron Spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}$ Complexes ($\text{L} = \text{SiCl}_3, \text{Si}(\text{CH}_3)_3$). D.L. Lichtenberger and A. Rai-Chaudhuri, *J. Am. Chem. Soc.*, **113, 2923-2930 (1991). (PRF)**

The He I and He II photoelectron spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiCl}_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)_3$ have been obtained in order to examine the bonding of silyl ligands to transition metals. The chemistry of both complexes has been studied previously in relation to models for catalytic intermediates in hydrosilation reactions. The nature of the metal-silicon σ bond and the possibility of π backbonding from the metal to empty silicon d orbitals are of particular interest to the understanding of this chemistry. Previous observations of unusually short Fe-Si bond lengths in this class of complexes have led to the proposal that silane ligands are good π -acceptors. However, the splitting pattern of the " t_{2g} -based" metal ionizations of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)_3$ shows no evidence of stabilization of metal d orbitals as would occur with π -backbonding to the silane. The splitting is essentially the same as observed in the spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$, where the hydride clearly has no π -acceptor capability. This same splitting is also observed in the spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$. A reduced splitting is observed in the spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiCl}_3$. Evaluation of these ionizations show that SiCl_3 is a better π -acceptor than CN and is about half as effective as CO at π stabilization of the metal ionizations. The π -backbonding to SiCl_3 probably involves significant portions of the Si-Cl σ^* orbitals. The short Fe-Si bond in the SiCl_3 complex is a combination of π -backbonding and ionic bonding contributions. The ionizations of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiCl}_3$ are also compared with the ionizations of the "isoelectronic" $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{-HSiCl}_3$ complex. The manganese complex is related to the iron complex by a "hydride shift" from the iron nucleus, and the ionization shifts help to reveal the extent of oxidative addition of the Si-H bond to the manganese center. The strength of the Mn-SiCl₃ bond contributes to the nearly complete oxidative addition of the Si-H bond to the metal. The implications of these results to the proposed mechanisms of hydrosilation reactions are discussed. The ionization trends in these complexes favor olefin insertion into the metal-silyl bond in the case of trialkylsilyl complexes.

4. Delocalized Electronic Interactions in Chiral Cyclopentadienyl Rhenium Halide Complexes. The Valence Photoelectron Spectra of $\text{CpRe}(\text{NO})(\text{L})\text{X}$ (Cp is $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5(\text{CH}_3)_5$, L is CO and $\text{P}(\text{C}_6\text{H}_5)_3$, X is Cl, Br, and I). 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). (DOE)

The He I photoelectron spectra of a series of $\text{CpRe}(\text{NO})(\text{L})\text{X}$ complexes (L is PPh_3 or CO; X is Cl, Br, I; Cp is $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_3$) 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 $\text{Re}(\text{I})$ metal 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 $\text{M-X } \pi^*$ orbitals have increasing halogen character from the chloride complex to the iodide complex. Unlike the previously studied $\text{Re}(\text{CO})_5\text{X}$ complexes, where the first ionization shifted from predominantly metal to predominantly halogen in proceeding from $\text{X} = \text{Cl}$ to $\text{X} = \text{I}$, in this case the first three ionizations remain predominantly metal throughout. There is indication in one case of further delocalized interaction of the $\text{M-X } \pi$ electrons with Cp-based electrons. The extent of delocalized and fluid electron density in these systems is in contrast to other systems like $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and $(\text{CO})_5\text{ReX}$.

5. 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). (DOE)

The Mg $\text{K}\alpha$ 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 are reported. The core XPS spectrum shows a single narrow carbon 1s ionization at 285.1 eV. The valence UPS spectra show very sharp valence

ionization bands, comparable to gas phase spectra, with wide separations between the lowest ionization energy features. The ionizations are consistent with theoretical calculations based on the highly symmetric truncated icosahedral structure. The first vertical ionization energy relative to the vacuum level is estimated to be 6.5 ± 0.2 eV from these solid state measurements.

6. **Modelling of the Intramolecular Structure of Monolayer C₆₀ 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, in *Clusters and Cluster-Assembled Materials*; R.S. Averback, J. Bernholc, D.L. Nelson, Eds.; *Mat. Res. Soc. Symp. Proc.*, **206**, 721-725 (1991). (DOE)

Images of monolayer coverages of C₆₀ on gold substrates, using scanning tunneling microscopy, reveal intermolecular arrangement and intramolecular features. In this paper we concentrate on the interpretation of these internal features, present a model showing that they arise from local charge density variations of high-lying π orbitals on approximately *every other carbon atom*, and discuss also other possible mechanisms for this effect.

7. **Multiple Bonds between Main-Group Elements and Transition Metals. 86. Methyltrioxorhenium(VII) and Trioxo(η^5 -pentamethylcyclopentadienyl)rhenium(VII): Structures, Spectroscopy, and Electrochemistry.** W.A. Herrmann, P. Kiprof, K. Rypdal, J. Tremmel, R. Blom, R. Alberto, J. Behm, R.W. Albach, H. Bock, B. Solouki, J. Mink, D.L. Lichtenberger, and N.E. Gruhn, *J. Am. Chem. Soc.*, **113**, 6527-6537 (1991). (DOE)

Two key compounds of organometal oxides, methyltrioxorhenium(VII) (**1**) and trioxo(η^5 -pentamethylcyclopentadienyl)rhenium(VII) (**2**), have been structurally characterized by means of electron diffraction techniques, showing that the ReO₃ fragments of these compounds have trigonal-pyramidal structures in the gas phase. The rhenium-carbon distance of the 14e complex **1** amounts to 206.0 (9) pm, which is the shortest Re-C(sp³) bond so far recorded. The pentamethylcyclopentadienyl derivative **2** has the longest known rhenium-carbon bond (240.5 (6) pm) due to the size of this particular π -bonded ligand and the σ/π -donor properties of the oxo ligands ("trans influence"). Infrared and Raman spectra show a much higher triple-bond contribution in the rhenium-oxygen bonds of **1** (force constant $k = 8.16$ mdyn/Å) compared with **2** ($k = 6.99$ mdyn/Å). The π -donor qualities of the ring ligand of **2** are considered the major effect to reduce the rhenium-oxygen bond order of this 18e compound since the σ -aryl complex (σ -C₆H₂Me₃)ReO₃ (**3**) has a force constant of $k = 8.08$ mdyn/Å. According to cyclovoltammetric data, the methyl derivative **1** is more easily reduced ($E_{pc} = -0.84$ V vs Ag/A,Cl, THF, 20°C) than the half-sandwich congener **2** ($E_{pc} = -1.72$ V), again

reflecting the electronic situation of the two compounds (14e vs 18e, respectively). The first vertical PE ionization energies of **1** and **2**, 11.8 and 8.6 eV, differ by 3.2 eV due to their different radical-cation ground states, Xa_2n_0 and $\text{Xe}, \pi_{\text{cp}}^*$). The equivalent oxygen lone pair type ionization of **2**, $\text{IE}_2^{\text{V}}(\text{a}_2, \text{n}_0) = 9.9$ eV, is lower by 1.9 eV and gives proof of the electron donation from the η^5 -bonded π -ligand C_5Me_5 . In addition, the PE spectrum of trioxo(η^1 -mesityl)rhenium(VII) (**3**) has been recorded: Its first ionization energy of 9.00 eV exceeds the corresponding one of mesitylene by 0.6 eV, thus demonstrating the considerable acceptor effect of the ReO_3 substituent group toward an η^1 -bonded π ligand. The high electric dipole moment of **2** ($\mu = 6.2$ D; benzene, 25 °C) appears reasonable in light of the high polarizability of the $\text{C}_5\text{Me}_5\text{-Re}$ bond (approximately 4 D); the ReO_3 unit has a dipole increment of ca. 2.2 D in **1** and **2**. NMR and PE spectra clearly show that the ReO_3 functionality is a strong electron-withdrawing substituent, stereoelectronically comparable with the SO_3H substituent in organic compounds.

8. Electronic Structure of Monodentate Coordinated Diphosphine Complexes. The Photoelectron Spectra of $\text{Mo}(\text{CO})_5(\text{P}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{CH}_3)_2)$ and $\text{Mo}(\text{CO})_5(\text{P}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2)$. D.L. Lichtenberger and M.E. Jatcko, *Inorg. Chem.*, **31**, 451-455 (1992). (DOE)

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 $\text{Mo}(\text{CO})_5\text{DMPE}$ and $\text{Mo}(\text{CO})_5\text{DMPM}$ and compared to the spectra of $\text{Mo}(\text{CO})_5\text{PMe}_3$ 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 $\text{PMe}_3 < \text{DMPE} < \text{DMPM}$. 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 .

- 9. 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.*, **B 9**, 2461-2465 (1991). (DOE)

Monolayer coverages of C_{60} on a gold substrate have been studied using scanning tunneling microscopy. The images reveal various packing arrangements and reproducible intramolecular contrasts of the C_{60} molecules. We find that *approximately every other carbon atom* is highlighted on the π -electron surface of the molecule as a result of a preferential electron transfer from the gold substrate, in agreement with a theoretical analysis of the high-lying π -electron density of a C_{60} molecule absorbed on metallic surfaces.

- 10. Buckyball-substrate Interactions Probed by Scanning Tunneling Microscopy and Atomic Force Microscopy.** D. Sarid, T. Chen, S. Howells, M. Gallagher, L. Yi, D.L. Lichtenberger, K.W. Nebesny, and C.D. Ray, *Ultramicroscopy*, **42**, 610-615 (1992). (DOE)

Submonolayers of buckyball molecules (C_{60}) on a gold substrate, deposited under ultrahigh vacuum (UHV) conditions, have been imaged in air using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). STM images show intramolecular contrasts within most individual C_{60} molecules. AFM images of the C_{60} molecules, often grouped in a hexagonal arrangement, show no atomic-scale features. A possible explanation for the presence or absence of the intramolecular contrasts in the images obtained with the STM and AFM, respectively, is given by a molecular orbital calculation.

- 11. High Resolution Images of Single C_{60} Molecules on Gold (111) Using Scanning Tunneling Microscopy.** S. Howells, T. Chen, M. Gallagher, D. Sarid, D.L. Lichtenberger, L.L. Wright, C.D. Ray, D.R. Huffman and L.D. Lamb, *Surface Science*, **274**, 141-146 (1992). (DOE)

The electronic interactions of fullerene molecules with metals, with other molecules, and with themselves are important to the chemical and conductive properties of these materials. We demonstrate high resolution scanning tunneling microscopy images of C_{60} molecules condensed on epitaxial gold (111) films on mica, in which the C_{60} molecules are isolated from each other. The C_{60} molecules were locked in position to the gold substrate by an ordered layer of methyl isobutyl ketone. The images of the C_{60} molecules exhibit

intramolecular contrast indicating a significant electronic interaction with the gold substrate. Current vs. voltage measurements show that both the C_{60} and the thin film of methyl isobutyl ketone have conductances comparable to that of the gold substrate.

12. 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, *Hot Papers of The Scientist*, **6(15)**, 16 (July 20, 1992). (DOE)

This was a highlight in the "Hot Papers" section of *The Scientist*. The original paper was the thirteenth most cited paper in all of the sciences in 1991. The paper first appeared in *Chemical Physics Letters*, **1991**, 176, 203-208. Prior to this work, the intriguing truncated icosahedral "soccer ball" structure of the C_{60} molecule had been surmised from detection of microscopic amounts of the molecule and from numerous theoretical calculations of the electronic structure and bonding. Following the synthesis of milligram quantities of C_{60} (Huffman), we set out to measure its full valence and core ionization spectrum. The ionizations provide the most direct experimental probe of the electronic structure of a molecule. The first significant observation was that, although the sixty carbon atoms provide sixty electrons to the valence pi ionization bands, only a few ionizations were observed in the valence energy region. This a consequence of the high symmetry of the molecule which, unlike any other molecule at the time, allowed for four-fold and five-fold degenerate electron energy levels. The first two separate valence ionization bands accounted for 28 of the 60 valence pi electrons. The spacing pattern of the valence ionizations agreed well with theoretical predictions. Thus the ionizations strongly supported the proposed "soccer ball" structure. Another significant result was the experimental measurement of the first ionization energy. Determination of this energy had been attempted previously by other experimental techniques and theories, with a wide range of results. The measurements reported in this paper are the foundation for numerous subsequent experimental and theoretical investigations of the properties of fullerenes.

13. The He I Valence Photoelectron Spectrum of C_{70} in the Gas Phase. D.L. Lichtenberger, M.E. Rempe and S.B. Gogosha, *Chem. Phys. Lett.* **198**, 454-460 (1992). (DOE)

The high-resolution He I photoelectron spectrum of C_{70} in the gas phase is reported and compared with that of C_{60} and theoretical calculations. Similar to C_{60} , the C_{70} spectrum shows two separate valence ionization band envelopes in the low energy region, but there are more separate ion states visible within the two envelopes. The first envelope of overlapping ionizations spans from about 7.3 to 8.8 eV, and the second from about 8.9 to 10.3 eV. The greater complexity of the C_{70} spectrum compared to that of C_{60} is expected

due to the lower symmetry of C_{70} and the ten additional pi electrons from the additional carbon atoms. The first vertical ionization energy is 7.47 ± 0.02 eV, which is destabilized 0.17 eV from that of C_{60} .

14. The Electronic Nature of the Metal-Metal Quadruple Bond: Variable Photon Energy Photoelectron Spectroscopy of $Mo_2(O_2CCH_3)_4$. D.L. Lichtenberger, C.D. Ray, F. Stepniak, Y. Chen and J.H. Weaver, *J. Am. Chem. Soc.* **114**, 10492-10497 (1992). (NSF)

Variable energy photoelectron spectroscopy of thin film $Mo_2(O_2CCH_3)_4$ on a GaAs substrate in ultra-high vacuum is used to examine the valence ionizations of the quadruple metal-metal bond. The changes in photoionization cross sections with photon energy over a range from 40-90 eV are examined. The metal-based σ , π and δ ionizations of the quadruple bond are strongly enhanced relative to the acetate-based ionizations in the region of photon energies from 40 to 50 eV. This is consistent with a molybdenum 4p to 4d resonance and super-Coster-Kronig Auger enhancement of the metal-based ionizations. The extent of resonance enhancement is related to the amount of Mo 4d character associated with the ionization. The π ionization of the Mo-Mo quadruple bond has the largest contribution from the Mo 4d orbitals. The δ and σ ionizations of the metal-metal bond contain smaller amounts of Mo 4d character, and some Mo 4d character is observed in the acetate-based ionizations. This is explained in terms of significant overlap and mixing of the δ and σ components with the ligand orbitals. Also, in the case of the σ component, there is a possible filled/filled interaction between the Mo 4d₂ orbital on one metal and the Mo 4p_z orbital on the adjoining metal. These interactions have significant impact on the properties of these complexes.

15. Electronic Structure and Bonding of C_{60} to Metals. D.L. Lichtenberger, L.L. Wright, N.E. Gruhn and M.E. Rempe, *Synthetic Metals* **59(3)**, 353-367 (1993). (DOE)

The electron distribution and orbital interactions of C_{60} with metals coordinated at different sites on the outside of the fullerene are evaluated with the Fenske-Hall molecular orbital method. The characters and nodal properties of the frontier orbitals of C_{60} are first evaluated in terms of basis transformations to the C_2 units that join the pentagons and to the C_5 units of the pentagons in the C_{60} molecule. The highest occupied molecular orbital (HOMO, h_u symmetry) of C_{60} is largely π bonding between the carbon atom pairs that join adjacent pentagons. The lowest unoccupied molecular orbital (LUMO, t_{1u} symmetry) is predominantly π antibonding between these carbon atom pairs. These orbital characters and energies are well-situated for synergistic bonding of a metal atom to the carbon-carbon pair between the pentagons, in which the HOMO of C_{60} donates sigma electron density to the metal, and the LUMO of C_{60} accepts pi electron density from the metal. The electron donation and acceptance between the individual molecular orbitals of the C_{60} molecule and the orbitals of a metal at different possible bonding sites of C_{60} is probed with a Ag^+ ion. It

is found that the bonding is favored at the site between the pentagons, and that many different orbitals of C_{60} are involved in the interaction. The net bonding of Ag^+ to C_{60} is weaker than to ethylene. Calculations are also carried out on the organometallic complexes $C_{60}Pt(PH_3)_2$ and $C_2H_4Pt(PH_3)_2$. The net bonding of ethylene and C_{60} to platinum is found to be very similar in these cases. A significant difference in this case is that the net negative charge on C_{60} is more delocalized in the carbon cluster in contrast to the localized charge on ethylene.

16. Metal-Acetylide Bonding in $(\eta^5-C_5H_5)Fe(CO)_2C\equiv CR$ Compounds. Measures of Metal $d\pi$ /Acetylide π Interactions from Photoelectron Spectroscopy. D.L. Lichtenberger, S.K. Renshaw, and R.M. Bullock, *J. Am. Chem. Soc.*, **115**, 3276-3285 (1993). (DOE)

Gas phase He I and He II photoelectron spectroscopy is used to experimentally determine the bonding interactions of η^1 -acetylide ligands in $(\eta^5-C_5H_5)Fe(CO)_2C\equiv CR$ compounds ($R = H, ^iBu$ or phenyl). Evidence of a large amount of interaction between the metal $d\pi$ orbitals and the acetylide $p\pi$ orbitals is obtained from the splitting of metal-based ionization bands, from the shifts in Cp-based and acetylide-based ionizations, from the changes in ionization cross sections between the He I and He II spectra, and from vibrational fine structure in the metal-based ionizations. The data indicates that the predominant π interactions between the acetylide ligands and the metal are filled/filled interactions between the occupied acetylide π bonds and the occupied metal $d\pi$ orbitals. From comparison of the electronic interactions of the $C\equiv CR$ ligands with the metal to those of CH_3 (a primarily σ donor ligand), halides (π donor ligands) and $C\equiv N$ (a weak π^* acceptor ligand) it is found that the metal-to-acetylide π^* backbonding is extremely small in the acetylide complexes. Varying the acetylide substituent causes significant changes in the σ and π donor properties of the $C\equiv CR$ ligand. Compared to $C\equiv CH$, the $C\equiv C^iBu$ ligand is a stronger σ donor ligand and also has a stronger filled/filled interaction between the metal $d\pi$ and acetylide π orbitals. The electronic mixing with the $C\equiv CPh$ ligand is even more extensive, since the metal $d\pi$ orbitals and the $C\equiv C$ π bonds are further mixed with the phenyl ring π orbitals. The nature of these π interactions helps to explain the observed reactivity of electrophiles with $ML_nC\equiv CR$ compounds and the observed electronic communication along the metal-carbon-carbon atom chain in transition metal acetylide compounds.

17. Electron Distribution and Bonding in η^3 -Cyclopropenyl-Metal Complexes. D.L. Lichtenberger, M.L. Hoppe, L. Subramanian, E.M. Kober, R.P. Hughes, D.S. Tucker and J.L. Hubbard, *Organometallics* **12**, 2025-2031 (1993). (DOE)

He I and He II photoelectron spectra of $(\eta^3-C_3R_3)Co(CO)_3$, $(\eta^3-C_3R_3)Ir(CO)_3$ and $(\eta^3-C_3R_3)Fe(CO)_2(NO)$ (where $R=t$ -butyl) are reported. The shifts and splittings in ionization energies with the metal and ligand

perturbations in this series, the changes in ionization peak areas as a function of the excitation energy, and Fenske-Hall molecular orbital calculations assist in the assignment and interpretation of the spectra. The cobalt complex reveals three peaks in the low ionization energy region that are primarily metal-based, consistent with the two states of e symmetry and one state of a_1 symmetry from the five d orbitals of a formally d^{10} metal in C_{3v} symmetry. The spectrum of the iridium complex has five peaks in this region due to large spin-orbit coupling that splits the e symmetry ionizations. The doubly degenerate peaks of the cobalt complex are also expected to be split in the photoelectron spectrum of the iron-nitrosyl complex due to the lowering of symmetry. Only four distinct peaks are seen for the iron-nitrosyl complex since two peaks at higher energy are merged in a broad envelope. The ionization cross sections indicate that the η^3 -bound C_3R_3 behaves formally as NO^+ , with a large amount of mixing and backbonding from the metal d_π orbitals to the e_{π^*} orbitals of the cyclopropenyl.

18. Correlations of Lone Pair Ionization Energies with Proton Affinities of Amino Acids and Related Compounds. Site Specificity of Protonation. S. Campbell, J.L. Beauchamp, M.E. Rempe, and D.L. Lichtenberger, *International Journal of Mass Spectrometry and Ion Processes*, **117**, 83-99 (1992). (DOE)

The gas phase proton affinities of amino acids are compared with their adiabatic ionization energies obtained from photoelectron spectra. Using primary aliphatic amines as reference species, a linear correlation is found between the proton affinities and the adiabatic nitrogen lone pair ionization energies for those amino acids which protonate on the amine group, even in cases where the nitrogen lone pair is not the highest occupied molecular orbital. Many of the amino acids fit the correlation well, which confirms the prediction of amine protonation from earlier studies and also corroborates the assignment of the bands in the complex photoelectron spectra of these species. Proline and sarcosine, amino acids with a secondary nitrogen, deviate from this correlation and instead fit a correlation using secondary aliphatic amines as reference species. Deviations from the correlation exist for molecules, such as lysine, methionine and tryptophan, which contain an intramolecular hydrogen bond between the basic side-chain and the amine site. The gas phase proton affinities of these species are larger than predicted by the correlation. Deviations from the correlation are also predicted for very basic amino acids, such as histidine and arginine, which protonate preferentially on the side-chain instead of the amine group.

19. Investigation of Metal- $d\pi$ Interactions in $(\eta^5-C_5H_5)(CO)_2Fe-C\equiv C-C\equiv CH$ using Photoelectron Spectroscopy. D.L. Lichtenberger, S.K. Renshaw, A. Wong, and C.D. Tagge, *Organometallics*, **12**, 3522-3526 (1993). (DOE)

The electronic structure of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-C}\equiv\text{C-C}\equiv\text{CH}$ (**1**) is investigated with gas phase He I and He II photoelectron spectroscopy (PES). A central issue is the electronic communication from the metal through the poly-yne chain. The spectra show distinct ionization bands (ionizations) that originate from the metal d^6 orbitals, the occupied butadiynyl π orbitals, cyclopentadienyl e_1'' orbitals, and the iron-butadiynyl σ bond. Metal- $d\pi$ -butadiynyl- π electronic interactions are indicated by the splitting pattern of the iron-based ionizations and from changes in ionization cross-sections from He I to He II excitation, which indicate the predominant character of ionizations. The $\text{C}\equiv\text{C-C}\equiv\text{CH}$ (butadiynyl) ligand is best described as a net π donor ligand, and in this case the occupied butadiynyl π orbitals interact with occupied metal $d\pi$ orbitals in filled/filled type interactions. The mixing between occupied metal $d\pi$ and butadiynyl π orbitals is extensive and the π system of **1** can be thought of as a five centered poly-yne. Results from Fenske-Hall and Extended Hückel calculations agree with the information obtained from PES, and also give additional information about orbital coefficients and charges of the $\text{C}\equiv\text{C-C}\equiv\text{CH}$ π system. The spectrum of **1** is also compared to that of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-C}\equiv\text{CH}$ and the separate σ and π bonding components of the $\text{C}\equiv\text{CH}$ and $\text{C}\equiv\text{C-C}\equiv\text{CH}$ ligands are evaluated.

20. Steric and Electronic Balance in Metal-Phosphine Coordination: The Phosphine Twist.

D.L. Lichtenberger and M.E. Jatcko, *J. Coord. Chem.* (Ted Brown Volume), submitted 9/93.
(DOE)

The relationship between the bite angles of *cis* phosphines and the electron distribution and bonding to the metal is studied by gas phase valence photoelectron spectroscopy. The complexes selected for the electronic structure comparison are *cis*- $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$, *cis*- $\text{Mo}(\text{CO})_4\text{DMPE}$, *cis*- $\text{Mo}(\text{CO})_4\text{DMPM}$, *cis*- $\text{W}(\text{CO})_4(\text{PMe}_3)_2$, *cis*- $\text{W}(\text{CO})_4\text{DMPE}$, and *cis*- $\text{W}(\text{CO})_4\text{DMPM}$. The Mo carbonyl complexes give simple photoelectron spectra with the valence ionizations originating from the phosphine lone pairs bonding to the metals and from the metal d^6 configurations. The W complexes give similar spectra, but have an additional electronic spin-orbit perturbation. The ionizations from the phosphine lone pairs that donate to the metals in σ bond formation show the effects of the different bite angles of the ligands. However, the total interaction and charge distribution of the phosphines with the metals looks very similar in each case. The metal-based ionizations also show very similar bonding and charge distribution in each case. The similarity of the *cis*-(PMe_3)₂ and *cis*-DMPE spectra is interesting in light of the $\approx 15^\circ$ difference in P-M-P angles. The metal-based ionizations of the *cis*-DMPM complexes are slightly different from those of the other complexes, primarily because of through-space interactions with the methylene carbon in the phosphine backbone. The similarity in electronic interactions with the metal in these complexes is traced to a *twist* of

the phosphine coordination to the metal which adjusts for the steric or bite angle constraints of the ligands with a minimum effect on the bonding to the metal. This results in slightly bent metal-phosphorus bonds.

21. **Proton Affinities and Photoelectron Spectra of Phenylalanine, N-methyl and N,N-dimethyl Phenylalanine. Implications for N-Methylation as an Approach to Charge Localization in Peptides.** S. Campbell, E.M. Marzluff, M.T. Rodgers, J.L. Beauchamp, M.E. Rempe, K.F. Schwinck, and D.L. Lichtenberger, *J. Am. Chem. Soc.*, **116**, 5257-5264 (1994). (DOE)

A Fourier transform ion cyclotron resonance (FT-ICR) technique for measuring gas phase proton affinities is presented which utilizes collisional dissociation of proton bound clusters by off resonance translational excitation. A simplified RRKM analysis relates unimolecular dissociation rates to proton affinities. This technique is used to measure values for the proton affinities of phenylalanine, N-methyl and N,N-dimethyl phenylalanine of 220.3, 223.6 and 224.5 kcal/mol, respectively (relative to the proton affinity of $\text{NH}_3=204$ kcal/mol). The proton affinity measured for phenylalanine is in excellent agreement with reported literature values. The photoelectron spectra of these three molecules are also presented and analyzed. Assignments of bands to specific ionization processes are aided by comparison with model compounds such as methyl substituted amines and 2-phenyl ethylamines. These data are employed to examine the correlation of adiabatic nitrogen lone pair ionization energies with gas phase proton affinities for phenylalanine, N-methyl and N,N-dimethyl phenylalanine in comparison to other amino acids and selected aliphatic amines. Amine nitrogen methylation has been identified as a technique for increasing the gas phase proton affinity of amino acids and localizing charge at the amine terminus of protonated peptides. The present study establishes that amine nitrogen methylation will not effect a sufficient increase in proton affinity to compete with protonation of some of the more basic side chains in peptides.

22. **Gas-Phase Ionization Energetics, Electron-Transfer Kinetics, and Ion Solvation Thermochemistry of Decamethylmetallocenes, Chromocene, and Cobaltocene.** M.F. Ryan, D.E. Richardson, D.L. Lichtenberger, and N.E. Gruhn, *Organometallics*, **13**, 1190-1199 (1994). (DOE)

The gas-phase free energies of ionization, ΔG_i° , for Cp^*_2Mn , Cp^*_2Fe , Cp^*_2Ni , Cp^*_2Os , Cp_2Cr , and Cp_2Co ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$, $\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) have been determined by using the electron-transfer equilibrium (ETE) technique and Fourier transform ion cyclotron resonance mass spectrometry. The high-resolution valence photoelectron spectra of bis(benzene)chromium(0), Bz_2Cr , Cp^*_2Os , and Cp^*_2Ru have also been measured. All ΔG_i° values are referenced to the estimated ΔG_i° value of Bz_2Cr , for which the narrow first ionization band at 5.473 ± 0.005 eV is assigned as the adiabatic

ionization potential. The ΔS_i° for ionization of Bz_2Cr is assumed to be equal to the electronic entropy change, $\Delta S_{elec}^\circ (= 1.4 \text{ cal mol}^{-1} K^{-1})$, and the difference between the integrated heat capacities for Bz_2Cr and Bz_2Cr^+ is also assumed to be negligible near room temperature ($\Delta H_{i,0}^\circ \approx \Delta H_{i,350}^\circ$), leading to $\Delta G_i^\circ(Bz_2Cr) = 125.6 \pm 1.0 \text{ kcal mol}^{-1}$. Through the use of thermochemical cycles, estimates are given for the average heterolytic and homolytic M-Cp bond disruption enthalpies of $Cp_2Cr^{+/0}$ and $Cp_2Co^{+/0}$. Cyclic voltammetry experiments ($CH_3CN/0.1 \text{ M Bu}_4NPF_6$) for the decamethylmetallocenes, including Cp^*_2Ru , were performed in order to determine differential solvation energies, $\Delta\Delta G_{solv}^\circ$, for the $+/0$ redox couples. Generally, $\Delta\Delta G_{solv}^\circ$ values for the decamethyl derivatives are in the range -21 to $-29 (\pm 4) \text{ kcal mol}^{-1}$. Electron-transfer kinetics for several metallocene couples were measured from the approach to equilibrium in the ETE experiments, and couples that involved Cp^*_2M compounds were observed to have rate constants $\sim 2 - 5\%$ of the Langevin collision frequency when the free energy change was in the range of 0 to -6 kcal mol^{-1} .

23. Sigma-Pi Interactions in Non-Conjugated Polyalkynes: A Photoelectron Spectroscopic

Study. Dennis L. Lichtenberger, Lalitha Subramanian, Uwe Bunz, and K. Peter C. Vollhardt, *J. Chem. Soc., Perkin Trans. II, J. Chem. Soc., Perkin Trans. 2*, 1351-1357 (1994). (DOE)

Through-space and through-bond interactions between π -orbitals in the molecules 1,6-heptadiyne (**A**), (3,3-diethyl)-1,4-pentadiyne (**B**), (4,4-dipropargyl)-1,6-heptadiyne (**C**), (2,2-dibromomethyl)-1,3-dibromopropane (**D**) and (4,4-diethynyl)-1,6-heptadiyne (**E**) are studied using gas-phase He I photoelectron spectroscopy. The assignments of the photoelectron bands are discussed in relation to the results of extended Hückel calculations. Mixing of the π orbitals with the σ bond framework of the molecules is revealed by broadened band profiles in the π ionization region. Detailed examination of the first ionization of **A** suggests that one conformation is predominant under the conditions of the experiment. The terminal π orbitals are separated by too great a distance for through-space interaction, so the spread of the ionization band is entirely from through-bond interactions. The low energy ionizations of **B** correspond to the in-plane and out-of-plane symmetric and antisymmetric combinations of the four terminal π orbitals, each of which has a different interaction with the C-H and C-C bonds of the central carbon atom. The spectra of **C** and **D** are very similar to each other, even though **C** has only alkyne substituents and **D** has only bromine substituents. The spectrum of **E** is a complicated mix of some of the features of **A** and some of the features of **B**. Extended Hückel calculations help clarify the number of orbitals in this region and the nature of the orbital interactions.

24. Electronic Structure of Exohedral Interactions Between C₆₀ and Transition Metals. Dennis L. Lichtenberger, Laura L. Wright, Nadine E. Gruhn, and Margaret E. Rempe, *J. Organomet. Chem.*, **478**, 213-221 (1994). (DOE)

The electron distribution and orbital interactions of C₆₀ with metals coordinated at different sites on the outside of the fullerene are evaluated. These sites include the position of a metal atom directly above a carbon atom (η^1 site), the metal atom centered above two carbons of a pentagon or above two carbons between two pentagons (both η^2 sites), the metal atom centered above a pentagon (η^5 site), and the metal atom centered above a hexagon (η^6 site). The frontier orbitals of C₆₀ are illustrated first with three-dimensional orbital contour plots. A palladium atom is then used to probe the bonding at the different sites on the C₆₀ surface. The results with Pd⁰ are compared to our earlier study with the harder Ag⁺ ion in order to examine the effects of metal electron richness and size. In addition, these results are compared with the bonding to more traditional ligands that represent the hapticity of these sites, such as methyl (η^1), ethylene (η^2), cyclopentadienyl (η^5), and benzene (η^6). The strength of the metal-C₆₀ interaction and the amount of charge delocalized from the metal to C₆₀ is sensitive to the site of coordination, the electron richness of the metal, and distortions in the geometry of C₆₀. As discussed in our previous work, the frontier orbitals of C₆₀ are well-suited for synergistic bonding of a metal atom to a carbon-carbon pair in an alkene-like fashion, in which the HOMO of C₆₀ donates carbon-carbon π bonding electron density to the metal, and the LUMO of C₆₀ accepts electron density from the metal into a carbon-carbon π^* antibonding orbital. Although the HOMO and LUMO of C₆₀ describe the basic interaction, many frontier orbitals are involved. The site above the C-C bond between two pentagons is favored over the site above the C-C bond within a pentagon, and the interaction above the other sites is indicated to be net repulsive by these calculations. The differentiation between these sites increases with the electron richness of the metal center. The bonding of the metal to C₆₀ is generally weaker than to the small ligands, except for very electron rich metal centers where the bonding to the η^2 site between pentagons apparently becomes stronger than the bonding to ethylene.

25. He I Valence Photoelectron Spectrum of C₆₀ in the Gas Phase. Dennis L. Lichtenberger and Margaret E. Rempe, *J. Chem. Phys.*, submitted 6/94. (DOE)

The high resolution He I photoelectron spectrum of C₆₀ in the gas phase at 380±10°C is reported. The C₆₀ was purified by chromatography and the spectrum gave no evidence of the presence of C₇₀ or larger fullerenes. It is shown that the spectrum reported previously from a sample that was presumed purified by controlled sublimation in the spectrometer actually included weak signals from C₇₀. The first ionization band (²H_u positive ion state) is examined in detail for the purpose of obtaining an accurate experimental measure of the first ionization energy. The analysis of the first band shape shows significant intensity from hot bands

on the low binding energy side corresponding to thermal population of the $\nu_1(a_{1g}, 496 \text{ cm}^{-1})$ breathing vibration in the ground state. The adiabatic ionization is determined to be $7.64 \pm 0.02 \text{ eV}$. The first vertical and adiabatic ionizations coincide, but the existence of short vibrational progressions at approximately $\nu_1(a_{1g}, 496 \text{ cm}^{-1})$ and $\nu_2(a_{1g}, 1469 \text{ cm}^{-1})$ indicates a small geometry change of the molecule with ionization. The progressions are represented reasonably well without significant changes in the vibrational energies from the ground to the positive ion state. There is evidence of a weak Jahn-Teller contribution on the order of the energy of the high-frequency vibration. The Jahn-Teller stabilization energy that is determined from the analysis of the ionization profile is the same as that predicted from theoretical calculations. The second ionization band is also examined in detail for vibrational information and for evidence of the presence of two different electronic states (2H_g and 2G_g) as predicted by theoretical calculations. This band gives one peak at 8.90 eV with hot bands as before, but no significant vibrational progression in the positive ion. A second peak in this band, at 9.14 eV , shows a vibrational progression similar to that discussed above. These peaks are assigned to the 2H_g and 2G_g states, respectively, on the basis of the characters of the h_g and g_g molecular orbitals.

B. Manuscripts Near Submission (from completed dissertations)

1. **The Electronic Structure and Bonding in *trans*-XW(CO)₄NO Complexes (X = Cl, Br, I) from Gas Phase Valence and Core Photoelectron Spectroscopy.** Dennis L. Lichtenberger, and Anjana Rai-Chaudhuri, (with John L. Hubbard, Department of Chemistry, Utah State University, Logan, UT 84322). (DOE)

He I, He II and Mg K α photoelectron spectra of a series of *trans*-XW(CO)₄NO complexes (X is Cl, Br, I) are reported. The high symmetry of these complexes and the combination of valence and core ionization spectroscopies provides direct quantitative information on trends in metal-halogen electronic interactions and the nature of the metal-nitrosyl bond. The He I/He II intensity trends are a valuable aid to the assignment of the valence ionizations and to the analysis of metal-ligand mixing. There is a filled-filled metal-halogen π interaction which increases on going from the chloride to the iodide. The first ionization of ClW(CO)₄NO has predominantly metal character whereas the first ionization of IW(CO)₄NO has similar metal and iodide character, signifying the greater metal-halide mixing in the higher halides. A comparison of the metal-halide π interaction in XW(CO)₄NO and XRe(CO)₅ complexes provides additional information on metal-nitrosyl bonding and the influence of the metal oxidation state. There is less metal-halogen mixing in the tungsten complexes compared to the rhenium complexes. The nitrosyl ligand in the tungsten complexes is *trans* to the halide and removes metal π electron density by backbonding, leading to the reduced metal-halogen π interaction. This observation is substantiated by Mg K α XPS studies which finds the oxygen 1s ionization

of the nitrosyl is destabilized to lower ionization energy than the corresponding oxygen 1s ionizations of the carbonyls. The Mg K α core ionizations of XRe(CO)₅ complexes have also been determined. Interestingly, both the valence and the core ionizations show that the charge potential at the metal does not change with substitution of the halogens down the series, presumably due to a balance of one-center and two-center charge effects.

2. The Electronic Structure, Bonding, and ¹³C NMR Chemical Shifts of Osmylated C₆₀.

Dennis L. Lichtenberger, Laura L. Wright and Margaret E. Rempe, (with Joel M. Hawkins and Stefan Loren, Department of Chemistry, University of California, Berkeley). (DOE)

The electronic structure of the osmylated C₆₀ derivative, C₆₀(OsO₄)(4-*tert*-butylpyridine)₂, is investigated with the aid of Fenske-Hall molecular orbital calculations. The electron distribution shows that the osmium metal of OsO₄ is reduced from a d⁰ to a d² configuration and the C₆₀ molecule is oxidized upon formation of the complex. The calculations also show a correlation between the contribution of each carbon atom to the LUMO and the upfield shift of that carbon atom in the ¹³C nmr.

3. Characterization of Metal-Carbon Multiple Bonds in Alkyne Metathesis Catalysts Using Photoelectron Spectroscopy. Dennis L. Lichtenberger, Martin L. Hoppe and Lalitha Subramanian. (DOE)

Photoelectron spectroscopic studies on the complexes I.(Me₃CC)Mo(CH₂CMe₃)₃, II.(Me₃CC)Mo(OCMe₃)₃, III.(Me₃CC)Mo(OCMe₂CF₃)₃, IV.(Me₃CC)Mo(OCMe(CF₃)₂)₃ and V.(Me₃CC)Mo(Cl)₃ reveal the HOMO to be primarily the Mo $\equiv$ C π bond. There is almost no change in the HOMO ionization energy when the alkyl ligands are replaced by alkoxide ligands while in the fluorine substituted alkoxide ligands, there is stabilization of all the ionizations indicating the metal center is becoming increasingly electrophilic. The average width of the first ionization band increases along this series from I to IV, indicating stronger interaction between the alkylidyne carbon and the Mo center. In the (Me₃CC)Mo(Cl)₃ complex, the increase in the relative intensity and the small width of the first ionization envelope are indicative of very significant electron density contributions from the chlorine atoms to the HOMO. Fenske-Hall molecular orbital calculations on model complexes are in agreement with the photoelectron spectroscopic assignment of the upper valence orbitals for this series of molybdenum complexes. Fenske-Hall calculation on the trichloride complex, V, shows approximately 40% chlorine character in the Mo $\equiv$ C (alkylidyne) π band. These observations provide insight into the reaction trends (with respect to alkyne metathesis) seen for these complexes. While there is very little alkyne metathesis product formed with (Me₃CC)Mo(CH₂CMe₃)₃ and (Me₃CC)Mo(OCMe₃)₃, the rate of alkyne metathesis reaction

increases with $(\text{Me}_3\text{CC})\text{Mo}(\text{OCMe}_2\text{CF}_3)_3$ and is best with $(\text{Me}_3\text{CC})\text{Mo}(\text{OCMe}(\text{CF}_3)_2)_3$. $(\text{Me}_3\text{CC})\text{Mo}(\text{Cl})_3$ complex does not yield any alkyne metathesis products. Alkyne metathesis can proceed either via a parallel attack or a perpendicular attack of the alkyne across the $\text{M}=\text{C}$ triple bond. The respective intermediates formed are either a metallacyclobutadienyl or a cyclopropenyl metal complex. The relative stabilities of the two alternate geometries is discussed.

4. Aspects of Bonding in Tetrathiapentalenes: A Combined Photoelectron and Theoretical

Investigation. Dennis L. Lichtenberger, Roy L. Johnston and Sharon K. Renshaw, (with Fred Wudl, Department of Chemistry and Physics, University of California, Santa Barbara, and Stefan Brode, Fritz Closs, Gerhard Krennrich and Lorenz Siggel, BASF AG, Federal Republic of Germany). (DOE)

He I photoelectron data are presented for three related thio and oxothio derivatives of tetrathiapentalene (1-3). Interpretation of the data is aided by *ab initio* and MNDO molecular orbital calculations. The calculations are used to explain structural distortions in 1. The broad ionization feature in the PES of 2 originates from the HOMO of 2 and is attributed to the removal of an electron from a S-S antibonding orbital, which leads to partial S-S bonding in the resulting cation. Tautomerization pathways are also discussed. A new tricyclic hexathiotrimethylenemethane C_4S_6 molecule (10) is postulated and predicted to be stable with a 2+ charge. All stable species discussed are found to possess 14 π electrons. Finally, the poor electron donor properties of these molecules relative to tetrathiafulvalene is explained in molecular orbital terms.

5. Electronic Structure and Relative Fe-H and Fe-CH₃ Bond Dissociation Energies of

$(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{R}$ Compounds ($\text{R} = \text{H}$ or CH_3) from Photoelectron Spectroscopy. Dennis L. Lichtenberger and Sharon K. Renshaw, (with R. Morris Bullock, Chemistry Department, Brookhaven National Laboratory). (DOE)

The electronic structure and bonding of FpH , FpCH_3 , Fp^*H and Fp^*CH_3 compounds (where $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ and $\text{Fp}^* = (\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2$) are investigated using gas phase He I photoelectron spectroscopy. The FpH compound serves as an excellent comparison for previously studied FpR compounds, where R is CH_3 , Cl , Br , I , SiR_3 and CN . The photoelectron spectra contain ionization bands that originate from the predominantly $\text{Fe}(\text{II})$ d^6 metal center, the cyclopentadienyl ring π system and the metal-ligand sigma bond. Trends in the spectra and Fenske-Hall calculations show mixing between Cp ring e set orbitals and the Fe-R sigma bond orbital, both of which utilize the "e_g" derived metal d orbitals in the pseudo-octahedral environment. Thus, the electron density in the metal-ligand bond is delocalized throughout the

molecule. The thermodynamic relationship between the ionization energy and bond dissociation energy (BDE) allows us to estimate the difference in metal-carbon and metal-hydride BDE for these bonds in FpR and Fp*R compounds. From the Fe-H and Fe-C sigma bond ionizations, we estimate that the M-H bond is 20 ± 2 kcal/mol more stable than the M-CH₃ bond in FpR compounds. The uncertainty in the relative bond strengths is partly due to mixing of the metal-Cp and metal-ligand bonds.

6. Study of the Electronic Distribution and Bonding in Ruthenocene and Substituted Ruthenocenes: The First Photoelectron Spectra of Perchloro- and Perfluorocyclopentadienyl Complexes. Dennis L. Lichtenberger, Yasser Elkadi and Nadine E. Gruhn, (with Russell P. Hughes and Owen J. Curnow, Department of Chemistry, Dartmouth College). (DOE)

The electronic structures of Cp₂Ru (Cp = η^5 -C₅H₅), Cp*CpRu (Cp* = η^5 -C₅(CH₃)₅), Cp*₂Ru, Cp*(C₅Cl₅)Ru and Cp*(C₅F₅)Ru are studied using gas phase photoelectron spectroscopy. The primary interaction of methyl groups as substituents on Cp ligands is a hyperconjugative effect which destabilizes the Cp and metal based ionizations in these complexes. The first example of gas phase photoelectron spectroscopy of perhalogenated Cp complexes is presented. Halide substituents show an admixture of inductive electron withdrawing and π electron donating effects, which balances to an overall slight electron withdrawing ability. The F substituent is only slightly more electron withdrawing than Cl as a Cp substituent.

7. Ligand-Mediated Metal-Metal Interactions in (η^5 : η^5 -fulvalene)bis(tetracarbonyl)cobalt and Rhodium Complexes. Dennis L. Lichtenberger and Margaret E. Rempe (with William E. Geiger and Teen T. Chin. Department of Chemistry, University of Vermont). (DOE)

Gas phase photoelectron spectroscopy (PES) is used to investigate the bonding in (fv)M₂(CO)₄ (fv = fulvalene, η^5 : η^5 -C₁₀H₁₀; M = Co, Rh). The PES of these bimetallic complexes are also compared to the previously reported PES of the analogous monometallic complexes, CpM(CO)₂ (Cp = η^5 -C₅H₅; M = Co, Rh). The ionization patterns observed for CpCo(CO)₂ and (fv)Co₂(CO)₄ are very similar, indicating that there is little electronic interaction between the two metals of the dicobalt complex. The spectrum of (fv)Rh₂(CO)₄ also appears as a doubling of the spectrum of CpRh(CO)₂, except that the first metal ionizations in the bimetallic rhodium compound show a significant splitting (0.45 eV). This splitting is due to electronic interaction between the two metal centers which occurs via communication through the fulvalene π system. As in the CpM(CO)₂ compounds, excited state relaxation energy effects are evident in the relative separation of ring ionizations when the metal is changed from cobalt to rhodium.

8. **The First Photoelectron Spectrum of a Disilene, Tetramesityldisilene. Detection of the Si-Si π Ionization and Comparison to Tetraphenylethylene.** Dennis L. Lichtenberger and Nadine E. Gruhn, (with Robert West, Nadia Comerlato and Honglae Sohn, Department of Chemistry, University of Wisconsin). (PRF)

Gas-phase photoelectron spectroscopy (PES) is used to investigate the bonding in tetramesityldisilene, $\text{Mes}_2\text{Si}=\text{SiMes}_2$ [$\text{Mes} = 2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_2$]. The PES of $\text{Mes}_2\text{Si}=\text{SiMes}_2$ is compared to that of the cyclodisiloxane $\text{Mes}_4\text{Si}_2\text{O}_2$ and tetraphenylethylene, $\text{Ph}_2\text{C}=\text{CPh}_2$ ($\text{Ph} = \text{C}_6\text{H}_5$). Fenske-Hall calculations are also reported for $\text{Ph}_2\text{Si}=\text{SiPh}_2$ and $\text{Ph}_2\text{C}=\text{CPh}_2$. The comparison of the disilene and alkene shows that the primary difference between the interaction of a $\text{C}=\text{C}$ π bond and a $\text{Si}=\text{Si}$ π bond with aryl substituents is the direction of the "push" of the filled-filled interaction with the π orbitals of the aryl. While for an alkene interaction with aryl groups stabilizes the $\text{C}=\text{C}$ π ionization, for a disilene this interaction destabilizes the $\text{Si}=\text{Si}$ π ionization. This difference is the direct influence of the difference in energy between $\text{C}=\text{C}$ and $\text{Si}=\text{Si}$ π bonds.

9. **Comparison of the Electronic Structure of Disilene, Silene, and Olefin Transition Metal Complexes.** Dennis L. Lichtenberger and Nadine E. Gruhn, (with Donald H. Berry, Department of Chemistry, University of Pennsylvania). (PRF)

Transition metal disilene, silene, and olefin complexes have been studied by gas phase photoelectron spectroscopy and molecular orbital calculations. Specific complexes which have been studied by photoelectron spectroscopy include $\text{Cp}_2\text{W}(\text{Me}_2\text{Si}=\text{SiMe}_2)$, $\text{Cp}_2\text{W}(\text{Me}_2\text{Si}=\text{CH}_2)$, and $\text{Cp}_2\text{W}(\text{H}_2\text{C}=\text{CH}_2)$. The energy separation between the ligand π -to-metal $d\pi$ ($1a_1$) orbital and metal $d\pi$ -to-ligand π^* (b_2) orbital of these complexes gets progressively smaller as the ligand is varied from olefin to silene to disilene. This is as would be expected from the π to π^* energy separations of unligated olefins, silenes, and disilenes. The first ionization of these compounds arises from the non-bonding $2a_1$ orbital of the formally d^2 metal center. The trend in first ionization energies is olefin < silene < disilene. When the positions of the first ionizations are corrected for the inductive effect of the methyl substituents on the silene and disilene compounds, the ordering switches to disilene < silene < olefin. Overall, the bonding in these compounds appears to be quite similar. Further studies of the electronic structure of these complexes, and correlation of electronic trends to chemical reactivity will be discussed.

10. **Comparison of the Bonding in Chelated Triphos and Tris(tertiary amine) Rhodium Complexes.** Dennis L. Lichtenberger and Lalitha Subramanian, (with Lin Wang and Thomas C. Flood, Department of Chemistry, University of Southern California). (DOE)

Various acidolysis reactions of (A) (Cn)RhMe₃ and (B) (3P)RhMe₃ [where Cn=1,4,7-trimethyl-1,4,7-triazacyclononane, 3P=CH₃C(CH₂PMe₂)₃] reveal large differences in their chemistries. Photoelectron spectroscopic studies on these systems provide insight into the nature of the HOMO and the differences in Rh-N and Rh-P bonding. The lowest ionization band in (Cn)RhMe₃ system is extremely narrow indicating the non-bonding nature of the metal d-orbitals. In contrast, in (3P)RhMe₃, it is consistently broad due to back-bonding interaction between the metal and phosphorus. The Rh-C σ bond in A is at 8.0 eV and that in B is at 10.0 eV the former can be broken more easily than the latter.

11. A Study of the Electron Configuration and Distribution in Rh₂(O₂CCF₃)₄. Dennis L. Lichtenberger and John R. Pollard (with F. A. Cotton, Texas A&M University). (NSF)

Most calculations on Rh₂(O₂CR)₄ give the formal electronic configuration between the metal atoms to be $\sigma^2\pi^4\delta^2\delta^*\pi^{*4}$, but there are disputes on this ordering, and specifically, the nature of the HOMO. Gas phase photoelectron spectroscopy has proven to be valuable in studying metal-metal bonded systems, but no previous gas phase photoelectron spectroscopic studies have been done on systems with the general structure Rh₂(O₂CR)₄ because most decompose readily upon sublimation. Rh₂(O₂CCF₃)₄ proved to be sufficiently stable and volatile for these experiments. The PES data collected suggests that the δ^* and π^* ionizations lie in the same first ionization envelope with the π^* being the HOMO, while the σ , π , and δ ionizations are located in the second group of ionizations. The first ionization band has a large cross-section with HeI excitation and falls substantially with HeII excitation. This indicates that the δ^* and π^* orbitals have a large amount of ligand character while the σ , π , and δ are more metal in character.

12. Extended Electronic Interactions in CpRe(NO)(L)R Complexes [Cp = η^5 -C₅H₅, η^5 -C₅(CH₃)₅; L = CO, P(C₆H₅)₃; R = H, CH₃]: Vibrational Analysis of Re-H Bond Ionizations and Comparison with Re-CH₃ Bond Ionizations. Dennis L. Lichtenberger*, Nadine E. Gruhn, Anjana Rai-Chaudhuri, and Sharon K. Renshaw (with John A. Gladysz*, Jeff Seyler and Alain Igau, Department of Chemistry, University of Utah). (DOE, NSF)

The electronic structures of CpRe(NO)(CO)R and Cp*Re(NO)(CO)R [Cp = (η^5 -C₅H₅), Cp* = (η^5 -C₅(CH₃)₅); R = H or CH₃] are studied using gas phase photoelectron spectroscopy. Comparison of the PES of the hydride and methyl compounds shows that the methyl ligand is acting as a π donor in these complexes. The comparison also shows mixing between the Cp and σ (Re-R) levels and suggests a delocalized sigma bonding framework. These results are supported by Fenske-Hall calculations. The larger shifts of the M1 ionization upon substitution compared to the other metal ionizations suggests that the d_{xz} orbital has been

rehybridized, leading to very efficient π overlap with the R ligands. This rehybridization is due to the differing abilities of the CO and NO ligands to remove electron density from the metal center. The first example of vibrational fine structure on metal-ligand σ ionization bands is observed on the Re-H sigma bond ionization band in the spectra of CpRe(NO)(CO)H and $\text{Cp}^*\text{Re(NO)(CO)H}$, and on the Re-D sigma bond ionization in the spectrum of the deuterium analog, $\text{Cp}^*\text{Re(NO)(CO)D}$. The vibrational progression corresponds to the frequency of vibration of the Re-H sigma bond in the molecular cation. Analysis shows that the Re-H bond lengthens by $\approx 0.24 \text{ \AA}$ when an electron is removed from the Re-H or Re-D sigma bond orbital. The PES of $\text{CpRe(NO)(PPh}_3\text{)}_3\text{R}$ and $\text{Cp}^*\text{Re(NO)(PPh}_3\text{)}_3\text{R}$ [$\text{Ph} = \text{C}_6\text{H}_5$] are also reported to illustrate the effect of CO substitution with PPh_3 in these complexes.

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

C. Dissertations

1. "Photoelectron Spectroscopy and Bonding of Iron and Rhodium Organometallic Compounds with Metal-Carbon and Metal-Hydrogen Bonds," Sharon Kintner Renshaw, University of Arizona, 1991 (*Diss. Abstr. Int. B* **1992**, 51(10) 5259).
2. "Photoelectron Spectroscopy of Dimolybdenum Tetracarboxylates: Probing the Electronic Nature of the Molybdenum-Molybdenum Quadruple Bond," Charles David Ray, University of Arizona, 1992 (M.S. thesis).
3. "Electron Donor and Acceptor Properties of Trimethylphosphine, Triphenylphosphine, and Related Ligands with Transition Metals by Photoelectron Spectroscopy," Margaret Eileen Rempe, University of Arizona, Ph.D. dissertation 1994.
4. "Electronic Structures of Unsaturated Silicon Compounds and Transition Metal-Silicon Interactions," Nadine Ellen Gruhn, University of Arizona, Ph.D. dissertation 1994.

III. PRESENTATIONS, 1991-1994

A. Invited

1. Ninth Biennial Carl S. Marvel Symposium, University of Arizona, Tucson, March 1991.
2. Garvan Symposium, 201st National Meeting of the American Chemical Society, Atlanta, GA, April 1991.
3. Gordon Research Conference on Organometallic Chemistry, Salve Regina College, Newport, RI, July 1991.
4. University of Texas, El Paso, September 1991.
5. Fullerene Symposium at The Electrochemical Society Meeting, Phoenix, AZ, October 1991.
6. University of Delaware, Newark, April 1992.

7. E.I. Dupont de Nemours and Co., Inc., Wilmington, Delaware, April 1992.
8. Gordon Conference on Inorganic Chemistry, July 1992.
9. AKZO Chemical, Dobbs Ferry, New York, September 1992.
10. University of California at Los Angeles, October 1992.
11. University of Southern California at Los Angeles, October 1992.
12. Arizona Fullerene Consortium, University of Arizona, November 1992.
13. University of Kentucky, November 1992.
14. Los Alamos National Laboratory, New Mexico, December 1992.
15. Arizona Fullerene Consortium, Arizona State University, Tempe, April 1993.
16. Theodore L. Brown Symposium, University of Illinois at Urbana-Champaign, August 1993.
17. Yale University, New Haven, CT, October 1993.
18. 1994 Gordon Research Conference on Inorganic Chemistry, Wolfeboro, New Hampshire, August 1994 (discussion leader).
19. 208th ACS National Meeting, Washington, DC, August 1994.

B. Contributed

20. "Intramolecular Structure and Two-dimensional Order of Monolayer C₆₀ 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.
21. "The Photoelectron Spectroscopy of C₆₀, 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.
22. "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.
23. "Electronic Structure and Bonding of Buckminsterfullerene, C₆₀, with Transition Metals," D.L. Lichtenberger, L.L. Wright, M.E. Rempe, C.D. Ray, S. Howells, T. Chen, M. Gallagher, D. Sarid; 203rd National ACS Meeting, San Francisco, CA, April 1992.
24. "Photoelectron Spectroscopy and Bonding of (η^5 -C₅H₅)Fe(CO)₂(C≡CR) Acetylide Compounds (R = H, CH₃, 'Bu), D.L. Lichtenberger and S.K. Renshaw, 203rd National ACS Meeting, San Francisco, CA, April 1992.
25. "Gas Phase Photoelectron Spectroscopy of C₆₀ and C₇₀," D.L. Lichtenberger and M.E. Rempe, 203rd National ACS Meeting, San Francisco, CA, April 1992.
26. "Photoelectron Spectroscopy of Substituted Pyridines and Imidazoles: A Measure of the σ - and π -Donor Abilities of Axial Ligands of Model Heme Compounds," D.L. Lichtenberger, F.A. Walker, N.E. Gruhn and A. Bjerke, 203rd National ACS Meeting, San Francisco, CA, April 1992.

27. "Photoelectron Spectroscopic Investigation of the Electronic Structure of η^3 -Cyclopropenyl Metal Complexes," D.L. Lichtenberger, M.L. Hoppe, L. Subramanian and E. Kober; 204th ACS National Meeting, Washington, D.C., August 1992.
28. "Vibrational Analysis of the Photoelectron Spectrum of C_{60} ," M.E. Rempe, M.E. Jatcko, D.L. Lichtenberger; American Physical Society National Meeting, Seattle, WA, March 1993.
29. "Electronic Structure of Tetramesityldisilene," D.L. Lichtenberger, N.E. Gruhn, R. West, N. Cormelato and H. Sohn; 205th ACS National Meeting, Denver, CO, March 1993.
30. "Metal-Hydride Versus Metal-Methyl Bonding in Chiral Cyclopentadienyl Rhenium Compounds," D.L. Lichtenberger, S.K. Renshaw, N.E. Gruhn, A. Rai-Chaudhuri, J.A. Gladysz, and A. Igau; 205th ACS National Meeting, Denver, CO, March 1993.
31. "Electronic Structure of Transition-Metal/Pyridine Interactions: Photoelectron Spectra of $Cp^*Mn(CO)_2L$ Complexes ($Cp^* = (\eta^5-C_5H_4(CH_3))$; $L =$ Pyridine or Substituted Pyridine)," D.L. Lichtenberger, N.E. Gruhn, A. Bjerke, S.B. Gogosha, C. Politte, and F.A. Walker; 205th ACS National Meeting, Denver, CO, March 1993.
32. "Characterization of Metal-Carbon Multiple Bonds in Alkyne Metathesis Catalysts Using Photoelectron Spectroscopy," D.L. Lichtenberger, M.L. Hoppe and L. Subramanian; 205th ACS National Meeting, Denver, CO, March 1993.
33. "Investigation of Group 5-Metal Bonding through Photoelectron Spectroscopy," D.L. Lichtenberger and M.E. Rempe; 205th ACS National Meeting, Denver, CO, March 1993.
34. "Trends in the Valence Ionization Energies of Substituted Ruthenocenes, $(\eta^5-C_5Me_5)(\eta^5-C_5R_5)Ru$, Where $R = H, Cl, \text{ and } F$," D.L. Lichtenberger, Y. Elkadi, R.P. Hughes, and O.J. Curmow; 205th ACS National Meeting, Denver, CO, March 1993.
35. "Nature of Bonding in d^3 - d^3 Metal Dimer Alkoxides," D.L. Lichtenberger, J.R. Pollard and T.M. Gilbert; 205th ACS National Meeting, Denver, CO, March 1993.
36. "Electronic and Structural Influences on Metal-Phosphine Bonding," D.L. Lichtenberger and M.E. Jatcko; 205th ACS National Meeting, Denver, CO, March 1993.
37. "Electronic Structure of C_{60} and its Derivatives," D.L. Lichtenberger, M.E. Rempe, N.E. Gruhn and L.L. Wright; 205th ACS National Meeting, Denver, CO, March 1993.
38. "Electronic Communication Between the Ligand and the Metal-Metal Bond: Photoelectron Spectroscopy of Para Substituted Dimolybdenum Tetrabenzoates," N.M. Carter, D.L. Lichtenberger and C.D. Ray; 205th ACS National Meeting, Denver, CO, March 1993, poster.
39. "Ozone and the Fullerenes: A Family Portrait," L.D. Lamb, D.L. Lichtenberger, Arizona Fullerene Consortium, Arizona State University, Tempe, April 1993.
40. "Geometry and Substituent Effects on the Electronic Structure of Disilenes," D.L. Lichtenberger and N.E. Gruhn; 206th ACS National Meeting, Chicago, IL, August 1993, poster.
41. "Electronic Structure and Bonding in Bimetallic Fulvalene Compounds," D.L. Lichtenberger and M.E. Rempe; 206th ACS National Meeting, Chicago, IL, August 1993, poster.
42. "Electronic Structure and Bonding in Bimetallic Fulvalene Compounds," D.L. Lichtenberger and M.E. Rempe; Evergreen State College, Olympia, WA, October 1993.

43. "Investigation of Sulfur Lone Pair Interactions in *cis* and *trans* Zwiebelane," D.L. Lichtenberger, E.E. Russell, J.R. Pollard, and R.S. Glass, Chemistry Undergraduate Symposium. (3rd place winner)
44. "Photoelectron Spectroscopy of Zwiebelanes," E.E. Russell; Honors Chemistry Minisymposium, University of Arizona, May 1994.
45. "Investigation of Metal-Ligand Conjugation in Metal-Acetylides," D.L. Lichtenberger, S.K. Renshaw and A.B. Uplinger, 9th DOE/BES Heterogenous Catalysis and Surface Chemistry Research Conference, Oconomowoc, WI, May 1994.
46. "The Electronic Effects of Cyclopentadienyl Ring Halogenation in Transition Metal Complexes," D.L. Lichtenberger, Y. Elkadi, N.E. Gruhn, J.R. Pollard, A.B. Uplinger, J.M. Dunworth, D.M. Crumpton, A.R. Kennedy, S.B. Gogosha, R.P. Hughes, O.J. Curnow and X. Zheng, 1994 Gordon Research Conference on Inorganic Chemistry, Wolfeboro, NH, August 1994, poster.
47. "The Controversial d^7 - d^7 Metal-Metal Bonds," D.L. Lichtenberger, J.R. Pollard and D.M. Crumpton, 1994 Gordon Research Conference on Inorganic Chemistry, Wolfeboro, NH, August 1994, poster.

IV. INSTRUMENTATION AND METHODS DEVELOPMENT

As discussed in the proposals and previous progress reports, the continuing improvement of our experimental and computational methods 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 more substantial developments of 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} sublimates 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 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 constructed a new chamber to increase the sample throughput for our experiments. This new chamber consists of a modified 8 inch cross pumped by a 170 l/s turbomolecular pump. It can have up to four independently controllable sources, either metal or organometallic, which are shuttered off to prevent mixing and premature deposition. The sample is mounted on a removable stub that can be heated via tantalum resistance heater or cooled from a liquid nitrogen dewar connected by a copper braid. Deposition is monitored by a quartz crystal microbalance and a quadrupole mass spectrometer is used to monitor background gases. Two other 8 inch ports will allow flexibility to add a reverse view LEED or RHEED system in the future. This system is capable of a base pressure of 5×10^{-10} torr with system bakeout. This gives us the ability to deposit a wide range of compounds including highly volatile compounds which require a low temperature stage as well as other compounds which may deposit epitaxially or in polycrystalline form on hotter substrates. This is of particular value in preparing samples that will be studied by scanning probe microscopy.

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.

C. Theory and Molecular Modeling Developments

We have continued to develop our methods for theoretical calculations of the electronic structure of transition metal complexes. Most significantly, I have written an extensive series of interactive programs for calculating and displaying two- and three-dimensional representations of molecular orbitals and total electron densities. The information provided by these programs has been extremely enlightening on the systems we are studying, and are becoming a standard part of our investigations. The program is extremely versatile, allowing Slater or Gaussian type basis sets and works with a variety of *ab initio* and semiempirical calculational methods. I have made the program (MOPLLOT2) generally available by placing it on the internet at the Ohio Supercomputing Center. Several people from around the world are already using the program. Another major accomplishment during this period has been the award from NSF to acquire new departmental minisupercomputers. These computers have been installed in recent months, and promise to greatly increase the sophistication of the theoretical calculations used in these investigations.

V. PERSONNEL (Postdoctoral Associates, Graduate Students, Undergraduates, Visiting Faculty, and Staff, * = current member)

1. Sharon K. Renshaw, DOE research associate, 1/15/87-7/9/93, reactivity of late-metal cyclopentadienyl complexes, ionization energy relationships with Hammett σ parameters, oxidative C-H bond additions, Ph.D. October 1991, bonding of acetylides in organometallics.
2. Dr. Laura Wright, Associate Professor, Furman University, NSF Research Opportunity Award visiting researcher, 6/24/91-6/15/92, STM of organic molecules on metals.
3. Lalitha Subramanian, NSF postdoctoral research associate, 8/27/91-2/18/94, early transition metal-metal bonds.
- 4.* Nadine Gruhn, NSF research associate, 1/1/90-12/1/94, metal-silicon bonds, Ph.D. December 1994, DOE postdoctoral research associate 12/1/95-present.
5. Mara Rempe, DOE research associate, 1/1/90-4/27/94, electronic structure of fullerenes, Ph.D. April 1994.
- 6.* John Pollard, NSF research associate, 1/1/92-present, late metal-metal bonds, has completed preliminary oral examination.
- 7.* Andrew Uplinger, DOE research associate, 1/1/93-present, metal acetylides, C-H bond activation, and substituted cyclopentadienyls, has completed preliminary oral examination.
- 8.* Joe Dunworth, DOE research associate, 1/1/94-present, early metal nitrides, carbynes and alkynes.

- 9.* Hua-Jun Fan, NSF research associate, 1/1/95-present, first year student, completed all qualifying examinations.
10. Charles Ray, NSF research associate, 1/1/90-6/1/92, surface studies of metal-metal bonds, M.S. May 1992.
11. Matthew Seidel, DOE/NSF undergraduate assistant, 5/11/89-12/20/91, construction of a new photoelectron spectrometer.
- 12.* Stefan Gogosha, DOE/NSF/PRF undergraduate assistant, 5/93-present, synthesis of new organometallic molecules for photoelectron spectroscopy.
- 13.* Erin Russell, volunteer undergraduate assistant, 1/94-present, photoelectron spectroscopy of sulfur-sulfur lone pair interactions.
14. Amy Bjerke, Research Experience for Undergraduates program, summer 1991, photoelectron spectroscopy of nitrogen heterocycles and porphyrins.
15. Melanie Nilsson, Research Experience for Undergraduates program, summer 1991, preparation of derivatives of buckminsterfullerenes.
16. Nancy Carter, Research Experience for Undergraduates program, summer 1992, extended electronic interactions in quadruple-bonded dimolybdenum benzoates.
17. Cecile Politte, Research Experience for Undergraduates program, summer 1992, electronic structure of substituted pyridines and imidazoles and interaction with metals.
18. Nancy Hull, undergraduate research associate, summer 1992, computer programming for photoelectron data collection and analysis.
19. Danielle Stines, Research Experience for Undergraduates program, summer 1993, synthesis of metallocene-olefin complexes.
20. Annette Suing, Research Experience for Undergraduates program, summer 1993, studies of highly volatile quadruple-bonded metal-metal complexes.
21. Dawn Crumpton, Research Experience for Undergraduates program, summer 1994, electron-rich multiple metal-metal interactions of late transition metals.
22. Abigail Kennedy, Research Experience for Undergraduates program, summer 1994, electronic effects of cyclopentadienyl perhalogenations with F, Cl, Br, and I.
- 23.* Professor Carl Baer, visiting Professor from Providence College, 1/5/95-6/30/95, extended electronic effects from substituted indenyls to early transition metal polymerization catalysts.
- 24.* Dona Myers, full time secretary serving this research group and the Enemark research group. Supported one-third by DOE funding and matched one-third by Professor Enemark and one-third by the Department.

VI. OTHER FUNDING AND PENDING SUPPORT

A. Current Research Support

United States Department of Energy; "Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding," March 1, 1992 - February 28, 1995; total award \$324,000.

National Science Foundation, CHE-9300841; "Ionization-Structure-Reactivity Relationships in Transition Metal Chemistry: Metal-Metal Complexes;" May 1, 1993 to November 30, 1996; total award \$332,000.

National Science Foundation; "Research Experience for Undergraduate Women in Material Chemistry," P.I. Jeanne Pemberton, with seven others; March 1, 1992 - February 28, 1995; total award \$120,000.

National Science Foundation; "Acquisition of a Workstation Cluster for Computational Chemistry," P.I. Neal Armstrong; (12 months) 1994; total award \$216,000.

B. Pending Research Support

none pending

C. Other Funding During This Period

American Chemical Society - Petroleum Research Fund; "Electronic Structure and Bond Energy Trends in Metal-Carbon and Metal-Silicon Chemistry," August 1, 1992 - August 31, 1994; total award \$43,000.