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

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PROGRESS REPORT

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MASTER

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ABSTRACT

The continued purpose of this research program is to obtain detailed experimental information on the different fundamental ways metals bond and activate organic molecules. Our approach has been to directly probe the electronic interactions between metals and molecules through a wide variety of ionization spectroscopies and other techniques, and to investigate the relationships with bonding modes, structures, and chemical behavior. During this period of the project we have (1) characterized the electronic features of diphosphines and monophosphines in their coordination to metals, (2) carried out theoretical and experimental investigations of the bonding capabilities of C_{60} to transition metals, (3) developed techniques for the imaging of single molecules on gold substrates that emphasizes the electronic backbonding from the metal to the molecule, (4) obtained the high resolution photoelectron spectrum of pure C_{70} in the gas phase, (5) compared the bonding of η^1 -acetylide ligands to the bonding of other small organic molecules with metals, and (6) reported the photoelectron spectra and bonding of η^3 -cyclopropenyl groups to metals. In each case, these are the first studies of their type.

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I. OVERVIEW AND PLANS FOR THE COMING YEAR

This report summarizes the results of this research in the recent seven month period ending September 30. The titles and brief reviews of the publications that were produced during this period are provided in the next section. This section will provide a few comments on this research and the directions for the coming year.

One direction in our work is the study of transition metal-phosphine complexes. Transition metal-phosphine complexes are important in many areas of homogeneous catalysis. Investigations of metal-phosphines (with differing R groups) are concerned with both the electronic interactions of the phosphines and with the steric size (Tolman cone angles). Paper number 1 in section II is our first detailed comparison of the electronic effects of diphosphines in the absence of steric effects. These diphosphines are coordinated with only one of the two phosphorus atoms that are capable of bonding to the metal center, as shown below.

In the next period of research we will extend this study to molecules in which both phosphorus atoms are bound to the metal atom. This introduces steric strain into the molecules and shows the effects of partial breaking of the bonds.

Several of the publications in section II document our progress in understanding the electronic structure of C₆₀ and its potential for bonding to transition metals. As pointed out in the previous report, the internal structures that we are able to observe by scanning tunneling microscopy of C₆₀ molecules deposited on a gold substrate give a spatial measure of electron donation from the gold surface to the molecule. The fourth paper in section II describes an approach we have discovered for observing single, separated molecules on gold by using a matrix of methylisobutylketone to help anchor the molecules. This may be a general approach with wide applications. We have already begun to make improvements in our equipment for these depositions in ultra-high vacuum, and intend to complete these improvements and study further applications of the approach in the next year.

Paper number 7 in section II reports the first high-resolution photoelectron spectrum of pure C_{70} in the gas phase. Our earlier paper on the photoelectron spectrum of C_{60} turned out to be the fourteenth most cited paper in all of the sciences in 1991, as shown in publication 5. We intend to continue examining larger fullerenes and derivatives of fullerenes as they become available.

Paper number 6 examines the different potential bonding sites of metal atoms or complexes to C_{60} . The figure at right shows some of the different possible sites, where the metal may be bound to a single carbon atom (site 1), to two carbon atoms in an η^2 fashion (site 2' or 2''), to five carbon atoms in an η^5 fashion (site 5), or to six carbon atoms in an η^6 fashion (site 6). There are organometallic analogues for all of these bonding situations. In the next period of the program we will continue characterizing the C_{60} -organometallic molecules that have been successfully prepared and look to making new derivatives of the fullerenes.

Paper number 9 compares the bonding of acetylide ligands ($-C\equiv CR$) with metals to the bonding of other small organic molecules such as CH_3 and CN with metals. Current interests in transition metal-acetylide compounds range from studies of basic chemical transformations with functionalized alkynes to investigations of non-linear optical and other special material properties. Questions remain about the bonding interactions of η^1 -acetylide ligands to metals that are important for understanding these properties. For example, electronic communication between the metal and the coordinated acetylide is suspected to be important in metallapolyynes, transition metal non-linear optical materials and bridging buta-1,4-diyne compounds, but the specific electronic interactions that would allow communication have not been directly evaluated. The iron system shows electronic mixing between the filled π symmetry orbitals, but no appreciable backbonding from the metal to the π^* acetylide orbitals. This is a point of controversy. We are now extending this to more electron rich metal centers like ruthenium-phosphine complexes to see if we can force backbonding from the metal to the ligand.

Paper number 10 characterizes the electronic structure and bonding of cyclopropenyl ligands to metals. Metal-cyclopropenyls, along with metallocyclobutadienes, are possible intermediates in alkyne metathesis reactions. Again, there has been controversy about the bonding and electronic structure of cyclopropenyls with transition metals. One basic question concerns the electron counting and formal oxidation state at the metal. This question is answered very clearly by the photoelectron studies.

The renewal proposal describes additional areas in which we are continuing to carry out investigations. In the coming year we are also continuing to develop the instrumentation and methods of these investigations. We have completed the upgrade of our surface instrumentation to new computer control, and are near to accomplishing the same with our gas phase photoelectron instrumentation, which will provide faster and more precise control of the experiments. Our new gas phase X-ray photoelectron spectrometer is completely assembled except for the magnetic shielding, and should become fully operational in the coming year.

II. TITLES AND ABSTRACTS OF RECENT PUBLICATIONS

1. **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).

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 .

2. **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).

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.

3. **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 (1992).

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.

4. **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).

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. voltages measurements show that both the C_{60} and the thin film of methyl isobutyl ketone have conductances comparable to that of the gold substrate.

5. **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).

This was a highlight in the "Hot Papers" section of *The Scientist* of one of our papers that turned out to be the fourteenth most cited papers 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.

6. **Electronic Structure and Bonding of C_{60} to Metals.** D.L. Lichtenberger, L.L. Wright, N.E. Gruhn and M.E. Rempe, *Synthetic Metals*, accepted.

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.

7. **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.*, in press.

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} .

8. **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.*, accepted 8/92.

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 $4d_{z^2}$ 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.

9. **Metal-Acetylide Bonding in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\equiv\text{CR}$ 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.*, submitted 8/26/92.

Gas phase He I and He II photoelectron spectroscopy is used to experimentally determine the bonding interactions of η^1 -acetylide ligands in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\equiv\text{CR}$ compounds (R = H, ^tBu 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 $\text{C}\equiv\text{CR}$ ligands with the metal to those of CH_3 (a primarily σ donor ligand), halides (π donor ligands) and $\text{C}\equiv\text{N}$ (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 $\text{C}\equiv\text{CR}$ ligand. Compared to $\text{C}\equiv\text{CH}$, the $\text{C}\equiv\text{C}^t\text{Bu}$ 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 $\text{C}\equiv\text{CPh}$ ligand is even more extensive, since the metal $d\pi$ orbitals and the $\text{C}\equiv\text{C}$ 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 $\text{ML}_n\text{C}\equiv\text{CR}$ compounds and the observed electronic communication along the metal-carbon-carbon atom chain in transition metal acetylide compounds.

10. **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*, submitted 9/92.

He I and He II photoelectron spectra of $(\eta^3\text{-C}_3\text{R}_3)\text{Co}(\text{CO})_3$, $(\eta^3\text{-C}_3\text{R}_3)\text{Ir}(\text{CO})_3$ and $(\eta^3\text{-C}_3\text{R}_3)\text{Fe}(\text{CO})_2(\text{NO})$ (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.

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