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Selected Topics in Organometallic Ion Chemistry

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Introduction

The tremendous growth of organometallic chemistry over the past two decades, spurred on in part by the desire to design more efficient catalysts, and bringing together researchers with diverse backgrounds in organic, inorganic, bioinorganic, and surface chemistry and catalysis, has been paralleled by a similar rapid growth in the area of gas-phase transition metal ion chemistry. Since the first observations of metal ion activation of saturated organic compounds by Allison, Freas, and Ridge,[1] naked metal ions,[2] ligated metal ions,[2] and small metal cluster ions[3] have been observed to be highly reactive and interesting species. Catalyzing this growth have been the spectacular advances in the types of mass spectrometry instrumentation which are being brought to bear on this problem. In addition, new and improved ionization methods have greatly expanded the types of systems that may be studied.

In analogy to the wealth of information pertaining to gas-phase organic ion chemistry, the study of transition-metal-containing ions offers the opportunity to probe the intrinsic chemical and physical properties of these species in the absence of complicating factors such as solvation and ion-pairing effects. In addition the gas-phase results provide benchmarks by which to compare detailed theoretical calculations. The chemistry of these highly electronically and coordinatively unsaturated species not only is interesting in its own right, but can provide important clues as to mechanisms occurring in condensed phases by yielding a better understanding of key steps and potential intermediates. Furthermore, obtaining quantitative data on the energetics of metal-ligand bonding and studying the periodic properties of metal ions as a function of their electronic structure are important in rendering organometallic chemistry a predictive science.

In this Account, several topics of current interest in the field are highlighted. Most of the discussion revolves around recent results from our laboratory using powerful FTICR methodology. Selected work from other laboratories is also included. Since the scope of this paper is necessarily limited, the reader is urged to read the outstanding comprehensive review

by Eller and Schwarz, as well as other excellent recent reviews on the subject.[2]

Fourier Transform Ion Cyclotron Resonance (FTICR) Spectrometry

The evolution of mass spectrometry instrumentation for applied analytical problems has brought with it the growing awareness that mass spectrometry can be an invaluable tool for studying the details of fundamental chemical problems. In this regard, FT-ICR[4] (also referred to as FTMS) must be considered one of the superstars, having evolved primarily as a method for studying fundamental ion-molecule processes. However, the virtually limitless mass range and astounding mass resolution, together with developing methodology resulting from an intense effort by several research groups, have also brought it to the forefront of analytical mass spectrometry.[5-18]

The key feature of FTICR for studying ion-molecule chemistry is the capability for manipulating the ion

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Professor Ben S. Freiser was born in Pittsburgh, PA, and attended UCLA, where he obtained his B.S. in chemistry summa cum laude in 1971 and was named to Phi Beta Kappa. He obtained his Ph.D. in 1977 from Caltech, where he studied the photochemistry of ions in the gas phase under the direction of Professor J. L. Beauchamp. While at Caltech he won the Herbert Newby McCoy Award in 1976. Ben joined the faculty of Purdue University in August 1976 and was promoted to associate professor in July 1982 and to professor in August 1985. He was the head of the Analytical Division from 1984 to 1988. He has published over 160 papers in the areas of gas phase ion chemistry and Fourier transform mass spectrometry and is the winner of numerous awards, including the 1985 ACS Award in Pure Chemistry.

and neutral populations. Because of the applied electric and magnetic fields, the trapping cell acts like an "electromagnetic bottle", permitting the storage of ions from milliseconds to hours. Thus, unlike conventional tandem mass spectrometers in which different experiments are performed in different locations along the ion trajectory, in FTICR the ions are generally confined spatially and MS^n experiments are carried out in time.[18] A pulse sequence under computer control runs the experiment with precise timing and can be readily modified as the experimentalist so desires. In our experiment the first pulse triggers a high-powered pulsed laser to generate metal ions by laser ablation from the pure metal target.[19] Following ion formation, a series of rf pulses of varied amplitude, frequency, and duration occur to effect three functions: (1) *selected ion ejection* to remove specific ions from the cell[20] (this function is key to determining reactant/product relationships and for isolation of targeted ions); (2) *collision-induced dissociation* (CID) used for ion-structure determination and as a tool for ion synthesis;[10,11,21] and (3) *detection*.[4,6] As long as ions remain in the cell, as many pulses as desired can be strung together in a sequence to manipulate and interrogate the ions. Several rf pulses can be consolidated by using powerful SWIFT excitation methods.[22] One or more neutral gases may be either leaked in or pulsed in at times specified by the pulse sequence.[13] As in a wet chemistry laboratory, the desired ions are synthesized, isolated, and permitted to react, and then the products are analyzed. This methodology has earned FTICR the nickname "the complete gas-phase chemical laboratory".

Chemical Ionization (CI)

In 1966 Munson and Field published their landmark paper introducing chemical ionization.[23] CI is a technique in which the sample is ionized by a reagent ion in an ion—molecule reaction. Unlike conventional electron impact, different reagent ions may be chosen to be as selective or "universal" as desired because the ionization process, as the name of the technique implies, is coupled to a chemical reaction. While early

work dealt primarily with protonating agents, which are still popular today, there is considerable work being done with other reagent ions taking advantage of the wealth of information available from fundamental ion—molecule reaction studies.[24] Included in this new group of reagent ions are atomic metal ions, which hold promise as selective CI reagents by offering a wide variety of reactivities.[25]

We have been active in this area, with the most recent example, described in brief here, being the use of metal ion CI as a simple, qualitative and potentially quantitative method for determining isotopolog and isotopomer distributions in partially deuterated cyclic hydrocarbons.[26] This study was in collaboration with my colleague Ian Rothwell at Purdue, whose group has been on the forefront in developing selective hetero- and homogeneous hydrogenation catalysts for aromatic molecules.[27] In order to determine the selectivity of the catalysts and understand the stereochemistry involved in the hydrogenation process, it was necessary to obtain detailed structural information on the selectively deuterated end products from the catalytic reactions.

Our analysis of the isotopolog distribution (molecules of a particular compound having a different number of isotopes) was based on attaching metal ions to the sample molecules either by direct condensation reaction 1 or by ligand displacement reaction 2, where L is an easily displaceable ligand such as ethylene.

$$M^+ + \text{sample} \rightarrow M(\text{sample})^+ \qquad (1)$$

$$ML^+ + \text{sample} \rightarrow M(\text{sample})^+ + L \qquad (2)$$
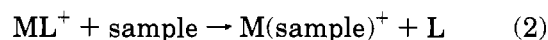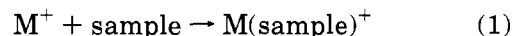
This procedure gives a series of pseudomolecular ions reflecting quantitatively the isotopolog distribution and providing information comparable to that obtainable from GC/MS. While GC/MS is excellent for determining the isotopolog distribution, however, it cannot provide information on isotopomers (molecules of a particular compound having the same number of isotopes in different configurations). This task can be accomplished by taking advantage of the intrinsic regioselectivity and stereoselectivity involved in the gas-phase dehydrogenation of cyclic hydrocarbons by transition-metal ions, namely, performing in the gas phase (dehydrogenation) the opposite process of that done catalytically in solution (hydrogenation).

To establish this approach, a known sample of selectively deuterated tetralin-d_8 was used. The tetralin-d_8 was synthesized in Rothwell's laboratory by catalytic hydrogenation of perdeuterated naphthalene.[28] GC/MS analysis showed that the sample consisted of >95% tetralin-d_8, $C_{10}H_4D_8$, and sophisticated high-resolution NMR and computer simulation

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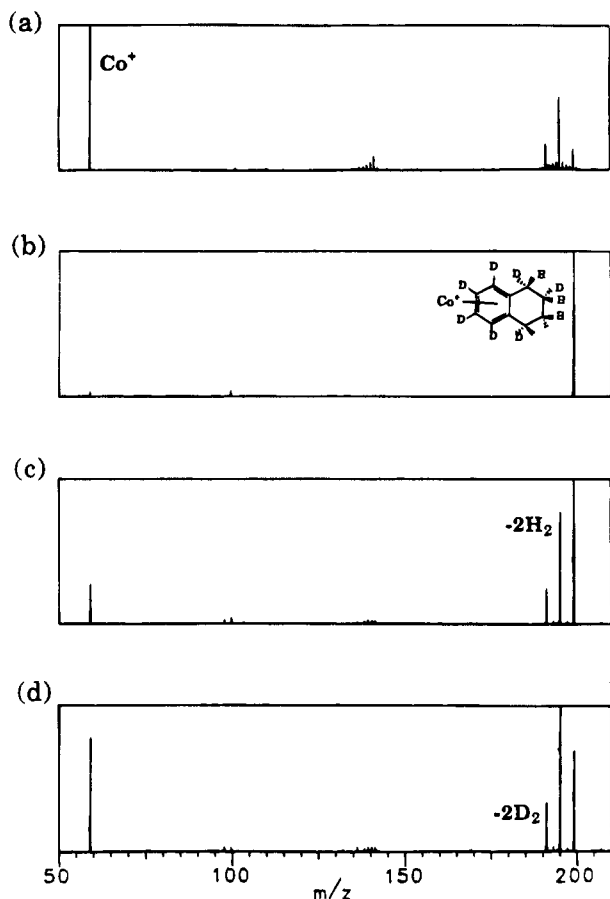
Figure 1. (a) Reaction of Co$^+$ with the tetralin sample. (b) Isolation of the Co$^+$–tetralin-d_8 isotopolog generated by the ligand displacement reaction of the tetralin-d_8 sample with Co-(alkene)$^+$. (c) CID on the isolated Co$^+$–tetralin-d_8 ion at 38 eV yields loss of 2H$_2$ and 2D$_2$ consistent with the all-cis structure **I**. (d) Same as spectrum c, but at 60 eV, indicating an increase in the formation of Co$^+$. Adapted from ref 26.

techniques indicated that the sample consisted primarily of the all-cis configuration, structure **I**.
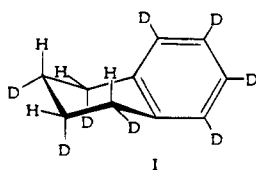


Ag$^+$, which is relatively inert due to its closed-shell d^{10} configuration, reacts with the tetralin sample by condensation, reaction 3, to form Ag(tetralin)$^+$. The

$$M^+ + \text{tetralin} \rightarrow \text{Ag(tetralin)}^+ \qquad (3)$$
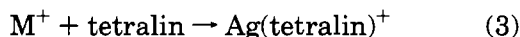
Ag$^+$ CI spectrum confirmed that tetralin-d_8 was the predominant isotopolog. Co$^+$ reacts with tetralin to form mainly the double dehydrogenation product ion, Co(naphthalene)$^+$, and a small amount of the Co-(tetralin)$^+$ condensation product, reactions 4 and 5, respectively. The predominant product peaks in Fig-

$$\text{Co}^+ + \text{tetralin} \longrightarrow \text{Co(naphthalene)}^+ + 2\text{H}_2 \qquad (4)$$
$$\longrightarrow \text{Co(tetralin)}^+ \qquad (5)$$
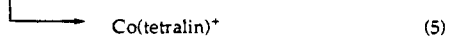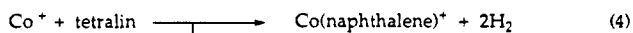
ure 1a, corresponding to CoC$_{10}$H$_4$D$_4$$^+$ and CoC$_{10}$D$_8$$^+$ and arising from the loss of 2D$_2$ and 2H$_2$, respectively, indicate a highly regio- and stereoselective process. In
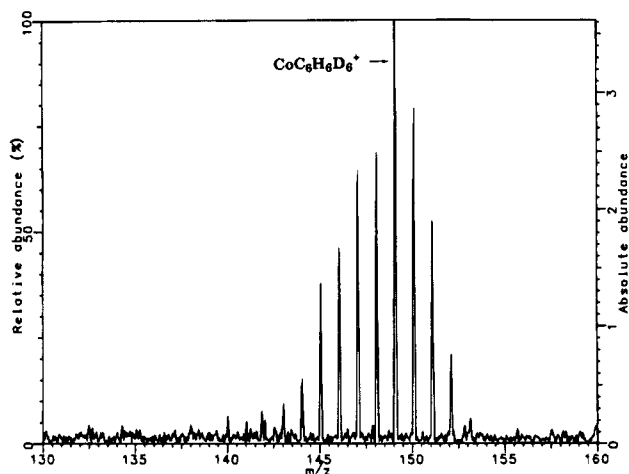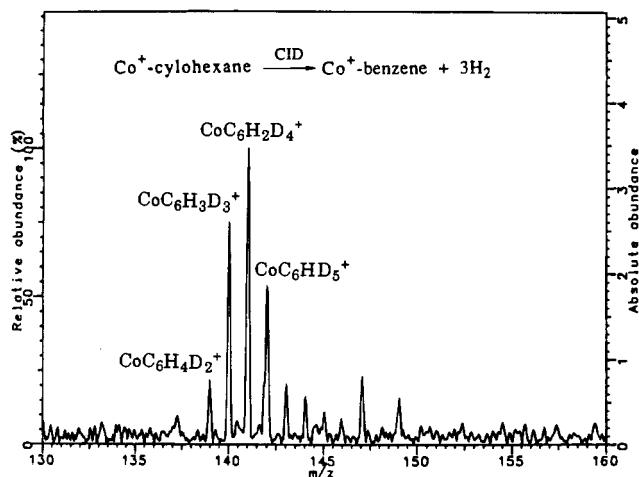

Figure 2. Isotopolog distribution of the partially deuterated cyclohexane sample obtained from the ligand displacement reaction of CoCO$^+$ with cyclohexane. Adapted from ref 26.

order to more clearly assess the degree of selectivity, the complication arising from the presence of albeit minor amounts of the other isotopologs (tetralin-d_7, tetralin-d_6, etc.) was circumvented by first isolating the Co(tetralin-d_8)$^+$ condensation product ion (Figure 1b) and then fragmenting it by collision-induced dissociation (Figure 1c,d). CID gives loss of 2H$_2$ and 2D$_2$, and at higher energies Co$^+$. The absence of HD elimination conclusively supports the assigned stereochemistry of structure **I** and confirms that, once dehydrogenation begins, the metal ion is restricted to one side of the ring. In this latter regard, the isotope ratio of about 3:1 observed instead of the expected equal loss of 2H$_2$ and 2D$_2$ is interesting and indicates a preference for initial C–H insertion over C–D insertion. These results are in accordance with a related study by Schwarz and co-workers.[29]

The metal ion CI method was next applied to a cyclohexane sample obtained from the heterogeneous hydrogenation of perdeuterated benzene.[28] CoCO$^+$ was found to be a good reagent ion for generating Co-(cyclohexane)$^+$ by a ligand displacement reaction. The resulting spectrum, Figure 2, indicates the presence of a broad distribution of isotopologs and, thus, that extensive scrambling occurs in the catalytic hydrogenation process. Isolation of the isotopolog CoC$_6$H$_6$D$_6$$^+$, followed by CID at energies sufficient to cause triple dehydrogenation, yields various deuterated Co(benzene)$^+$ species from which the isotopomer distribution can be deduced. As seen in Figure 3, for example, CoC$_6$H$_6$$^+$ and CoC$_6$D$_6$$^+$ arise from loss of 3D$_2$ and 3H$_2$, respectively, from the all-cis isotopolog, while CoC$_6$-H$_2$D$_4$$^+$ and CoC$_6$H$_4$D$_2$$^+$ arise from the isotopomer having two deuteriums on one side and four on the other. Again, isotope effects are evident. The presence of CoC$_6$H$_3$D$_3$$^+$ is significant in demonstrating that not all of the scrambling occurs two hydrogens (or deuteriums) at a time.

Compared to NMR techniques, this method requires far less sample, is quicker and easier to interpret, and easily detects components of low concentration which might be obscured by the major species in NMR. In addition, while the presence of more than one isotopomer or abundant other isotopologs renders the NMR

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Figure 3. CID at 32 eV on $CoC_6H_6D_6^+$ isolated from the isotopolog distribution shown in Figure 2. Triple dehydrogenation yields various deuterated $Co(benzene)^+$ species, which indicate the presence of several isotopomers. Adapted from ref 26.

experiment virtually impossible, the CI method is still applicable.

Metal—Ligand Bond Energies

One of the great successes of the work in this field has been to create a large, and ever-growing, data base on metal ion—ligand bond energies and related thermochemistry.[30] While only a relatively few values were known for $D(M^+-L)$ and $D(M-L)$ in the early 1980s, today several thousand experimental and theoretical values are available. The importance of transition metal—ligand bond energies, and in particular metal—hydrogen and metal—carbon bond energies, in such areas as homogeneous catalysis, surface chemistry, biochemistry, and other areas has provided much of the impetus for studying gas- and condensed-phase organometallic thermochemistry.[30] Closer to home, determining whether a proposed mechanism for an observed metal ion reaction is energetically feasible requires a knowledge of metal—ligand bond energies.

Several powerful gas-phase techniques have been developed over the years for these measurements. Among these, the determination of endothermic reaction thresholds by guided ion beam techniques has yielded the majority of the experimental absolute values currently in the literature.[32] In these experiments, pioneered by Armentrout and Beauchamp for metal ion systems, a mass- and energy-selected ion beam is collided with a reagent gas under single-collision conditions. Monitoring the product ion intensity as a function of ion kinetic energy and using a sophisticated data analysis procedure, one can accurately determine the endothermicity of the reaction, from which the bond energy information is obtained. Experiments analogous to the ion beam approach have also been reported using triple-quadrupole instruments[33] and FTICR mass spectrometers.[34]

Several methods have been developed for obtaining bond energy information using FTICRMS.[35] In addi-

tion to the analogy to the ion beam experiment, mentioned above, ligand-displacement reactions and equilibrium measurements yield accurate relative and absolute bond energies. Observation of exothermic ion—molecule reactions (reactions that proceed at $\geq 10\%$ efficiency) can provide energy limits. Competitive ligand loss by collision-induced dissociation, developed by Cooks and co-workers,[36] has shown promise for yielding both qualitative and quantitive bond energy information, and finally, photodissociation threshold measurements in many instances yield absolute metal—ligand bond energies.[37]

Another powerful technique involves the use of a reverse-geometry double-focusing mass spectrometer to measure the kinetic energy release distributions (KERD) of product ions formed in metastable decompositions.[38] In the absence of collisions, metal ion complexes formed in the ion source containing excess internal energy may dissociate in the second field free region between the magnetic and electric sectors. The distribution of internal energies leads to a broad metastable peak, which can be analyzed to yield, in many cases, absolute bond dissociation information. The KERD method is complementary to the ion beam experiments in that it provides data on exothermic reactions, while the ion beam experiments monitor thresholds for endothermic reactions.

Until relatively recently, theoretical calculations on transition metal—ligand systems were not available or not reliable. This situation has dramatically changed with rapid improvements in both methodology and computer architectures. Bauschlicher and co-workers[39] have been particularly active in this area in their calculations on various cationic species, while Siegbahn and co-workers[40] have focused on neutral systems. Others active in the area include Harrison[41] and Goddard[42] and their co-workers. The calculations have gotten to be so reliable, under the proper circumstances, that many times discrepancies between theory and experiment are found to be due to experiment. In addition they are the gas-phase equivalent to X-ray structure analysis in providing optimal geometric parameters. The combination of theory and experiment will continue to enjoy a particularly synergistic relationship in this field.

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A logical extension to understanding the activation of C—H and C—C bonds by bare transition-metal ions

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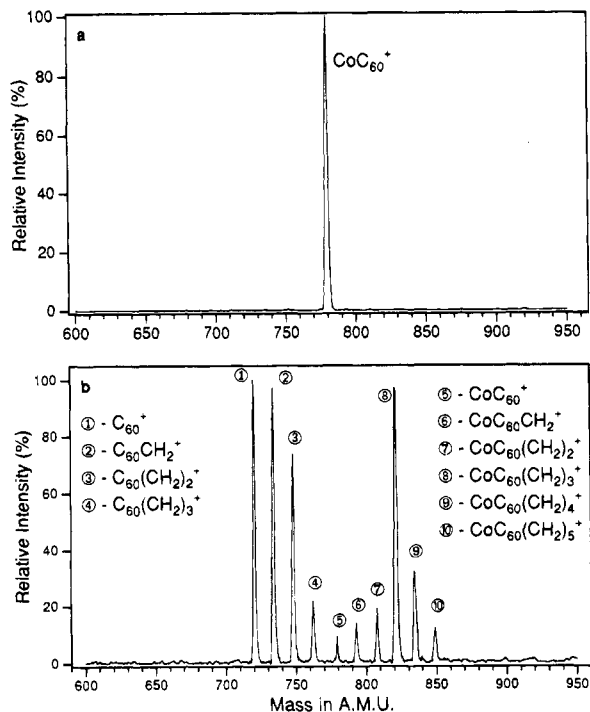
Figure 4. (a) Isolation of CoC_{60}^+ using ion ejection techniques. (b) Pulsing in cyclopropane to a maximum pressure of on the order of 5×10^{-5} Torr, then allowing an 800 ms delay.

is to study the effects that ligands bound to the metal center have on the gas-phase metal ion reactivity. Once again, this permits the study of the "intrinsic chemistry" in the absence of complications due to solvation and the presence of other ligands. This has been an active area of gas-phase metal ion research covering a wide variety of metals and ligands.[2] Of our most recent examples, C_{60} as a ligand is among the most currently relevant and provides a simple illustration of this type of study.[43]

Buckminsterfullerene, C_{60}, first discovered as an intense, "magic" peak in a mass spectrum,[44] has caught the attention not only of scientists but also of the public. The development of new materials and new compounds based on C_{60} and other fullerenes is currently an area of intense study.[45] Along these lines, gas-phase ion–molecule reactions involving C_{60} may provide clues to stable compounds that could be synthesized in the condensed phase, and they are interesting in their own right.[47-49]

Our initial work in this area was to demonstrate that externally bound (exohedral) MC_{60}^+ complexes[49] could be distinguished from endohedral complexes, in which the metal ion is encapsulated in the C_{60}.[50] Although Smalley and co-workers had provided good evidence that the MC_{60}^+ species generated in their

supersonic source were endohedral complexes,[50] it was not unequivocal.[51] Like C_{60} itself, these materials initially were, after all, just peaks in a mass spectrum and not available for analysis in macroscopic amounts. Thus, when gram quantities of C_{60} became available,[52] we were excited to apply FTICR to the problem.
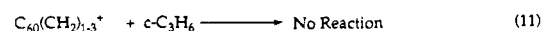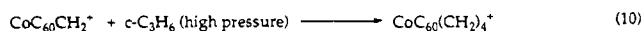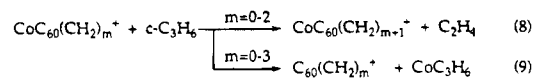
Our recent studies focus on C_{60} as a ligand, where we are particularly interested in the effect it has on metal ion reactivity and whether the derivatization of C_{60} can be catalyzed by the metal center. Typifying this work is a study of the reactions of CoC_{60}^+ with some simple C_2-C_4 hydrocarbons.[43] CoC_{60}^+ undergoes a condensation reaction with background C_{60} to form $Co(C_{60})_2^+$ and with pulsed in ethene, propene, 1-butene, and isobutene to form $C_nH_{2n}CoC_{60}^+$, exclusively (reaction 6 for $n = 2-4$). These $C_nH_{2n}CoC_{60}^+$ ions undergo

$$CoC_{60}^+ + C_nH_{2n} \rightarrow C_nH_{2n}CoC_{60}^+ \qquad (6)$$
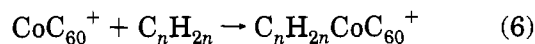
ligand displacement reaction 7 with C_{60} to form $Co(C_{60})_2^+$ and, upon CID, yield CoC_{60}^+ and C_{60}^+. Both of these results strongly suggest that the alkenes are coordinated to the metal center.

$$C_nH_{2n}CoC_{60}^+ + C_{60} \rightarrow Co(C_{60})_2^+ + C_nH_{2n} \qquad (7)$$
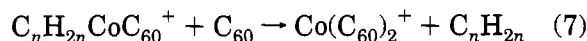
In contrast, CoC_{60}^+ reacts slowly with cyclopropane to generate two sets of products, metalated $CoC_{60}(CH_2)_{1-3}^+$ and unmetalated $C_{60}(CH_2)_{0-3}^+$, Figure 4. $CoC_{60}(CH_2)_{4,5}^+$ species were also observed but only under high-pressure conditions. Reactions 8–11 were determined by ejection techniques. Evidence that

$$CoC_{60}(CH_2)_m^+ + c\text{-}C_3H_6 \xrightarrow{m=0-2} CoC_{60}(CH_2)_{m+1}^+ + C_2H_4 \qquad (8)$$
$$\xrightarrow{m=0-3} C_{60}(CH_2)_m^+ + CoC_3H_6 \qquad (9)$$

$$CoC_{60}CH_2^+ + c\text{-}C_3H_6 \text{ (high pressure)} \longrightarrow CoC_{60}(CH_2)_4^+ \qquad (10)$$

$$C_{60}(CH_2)_{1-3}^+ + c\text{-}C_3H_6 \longrightarrow \text{No Reaction} \qquad (11)$$

$CoC_{60}(CH_2)_{1,2}^+$ ions involve coordination of buckminsterfullerene derivatives to Co^+ is 2-fold: CID of these ions yields the unmetalated species $C_{60}(CH_2)_{1,2}^+$, and reaction with C_{60} yields the condensation product $C_{60}CoC_{60}(CH_2)_{1,2}^+$, exclusively, in contrast to ligand displacement reaction 7. CID of the $C_{60}(CH_2)_{1-3}^+$ buckminsterfullerene derivatives, generated in reaction 9, yields C_{60}^+, exclusively, indicating that the CH_2 moieties in $C_{60}(CH_2)_{2,3}^+$ are bonded together to form a four-membered and a five-membered ring with C_{60}, respectively. In addition, CID and ligand displacement with C_{60} indicate that the $CoC_{60}(CH_2)_3^+$ species consists of two isomers, $\sim60\%$ $CoC_{60}(CH_2)_3^+$ and $\sim40\%$ $C_3H_6CoC_{60}^+$, while the $CoC_{60}(CH_2)_4^+$ species consists of 100% $C_3H_6CoC_{60}CH_2^+$.

In reaction 9, the neutral product is written as a CoC_3H_6 complex, as opposed to $Co + C_3H_6$, because energy is required to remove Co from $CoC_{60}(CH_2)_{0-3}^+$ to form the unmetalated analog. Reactions 12 and 13 provide the bond energy bracket $D(Co^+-benzene) = 68 \pm 5$ kcal/mol[38] $> D(Co^+-C_{60}) > D(Co^+-propene) = 44 \pm 2$ kcal/mol.[53] This in turn yields $D(Co-C_{60}^+) > 38 \pm 2$ kcal/mol based on the difference $IP(C_{60}, 7.61$ eV)[54] $- IP(Co, 7.684$ eV)[55] $= -0.254$ eV (~-6 kcal/

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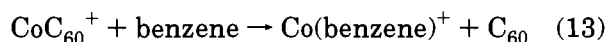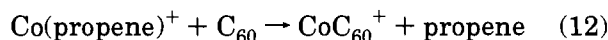(45) *Acc. Chem. Res.* **1992**, *25*, 97–176.

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$$Co(propene)^+ + C_{60} \rightarrow CoC_{60}^+ + propene \quad (12)$$

$$CoC_{60}^+ + benzene \rightarrow Co(benzene)^+ + C_{60} \quad (13)$$

mol). Thus $D(Co-C_3H_6) \geq D(Co-C_{60}^+) > 38 \pm 2$ kcal/mol. This limit is reasonable on the basis of the available data such as $D(Ni-C_2H_4) = 35.2 \pm 4.2$ kcal/mol,[56] determined experimentally, and $D(Rh-CH_2-CH_2CH_2) = 40$ kcal/mol, obtained by calculation.[57] Demetalation reactions analogous to reaction 9 have been previously reported.[58] Other derivatization reagents are currently being tested.

Excited-State Metal Ion Chemistry

Just as studying the periodic properties of metal ions has provided insight into the effect of electronic structure on reactivity and bond energies,[31,54] studying a single metal ion in its ground and various electronically excited states can provide further information along these lines. In addition it is clearly important to know the state of the ion, if accurate thermochemical information is to be derived. In most cases, suppression of excited-state ions is desired and various collisional and radiative cooling procedures are used. They are not always 100% effective, however, and therefore, caution is advisable in assuming ground-state behavior. Generation and characterization of the reactivity of excited-state metal ions has recently become an active area of research.

Excited-state metal ions can be detected by observation of normally endothermic reactions. The earliest study reported was performed by Freas and Ridge, who noted that a fraction of the Cr^+, generated by electron impact on $Cr(CO)_6$, reacted with CH_4 in an ICR spectrometer to form the endothermic product $CrCH_2^+$.[60] Further study indicated that as much as 75% of the population starts out in the excited state.[61] In a later study Strobel and Ridge[62] using FTICR showed that about 22% of the Mn^+ produced by electron impact on $Mn_2(CO)_{10}$ are in electronically excited states and used a time-delay method to measure a lifetime of $\geq 5.8 \pm 0.75$ s. More recently, Oriedo and Russell[63] have extended this methodology by monitoring the charge-exchange reactions of metal ions (generated in various ways) with their corresponding metal carbonyl compounds. Likewise, we have found SF_6 to be an interesting and useful reagent for these types of studies.[64]

Armentrout and co-workers[65] have studied a number of state-specific reactions using the ion beam apparatus. When the ion source conditions are varied, the amounts of excited electronic states present in the reactant ion beam are altered, enabling a deconvolution of the excited state/reactivity relationships. These investigators have documented dramatic effects on metal ion reactivity with hydrogen, ammonia, small hydrocarbons, and most recently, silane.[65c]

Bowers and co-workers[66] have developed a gas-phase ion chromatography technique which is remarkable in both its simplicity and its applications to a whole range of interesting problems. Mass-selected ions are pulsed into a reaction cell containing a buffer gas and drifted axially under the influence of a weak electric field. Ions which interact less with the buffer gas will have a higher mobility. For example, because the 4s orbital is larger than the 3d orbital, the $4s3d^{n-1}$ metal ion configurations have a more repulsive interaction with the bath gas than the $3d^n$ configurations, and they drift more rapidly. In analogy to conventional chromatography, the ground- and excited-state populations can be determined from the corresponding peak areas of the chromatogram. Furthermore, state-specific rate constants can be measured, as well as collisional relaxation dynamics.

Weisshaar and co-workers,[67] using elegant multiphoton ionization methods, have been able to generate and study pure populations of Fe^+ and V^+ ground and excited states, including specific J levels! They have shown, for example, that the $^4F_{5/2}(3d^7)$ state reacts about twice as fast as the 7/2 and 9/2 states. Unfortunately, while these experiments are the ultimate in state specificity, they are limited to only a few metals.

The work in this area, together with high-level ab initio calculations, has pointed to the importance of factors such as conservation of spin, the electron-donating and -accepting capability of the metal ion, the presence of low-lying electronic states of the metal of the correct symmetry and spin, orbital occupancy, and orbital hybridization in the activation of σ bonds by transition metals.

Doubly-Charged Ions

While there is an extensive literature on the gas-phase chemistry of singly-charged metal-containing ions, chemists and particularly solution chemists are likely to inquire about the reactivities of multiply-charged species. After all, Fe^{2+} and Fe^{3+} are the stable oxidation states of iron in solution and not Fe^+. Studies on doubly-charged alkaline earth metal ions date back to the 1960s and are relatively numerous, since these ions can be readily generated by thermal ionization due to their relatively low work functions.[68] Transition-metal ions are not as amenable by this method. Over the past 10 years, however, there has been a steady increase in the number of studies in this area, promoted by the development of new and convenient ways for generating multiply-charged transi-

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Organometallic Ion Chemistry

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tion-metal ions. Of particular promise is the electrospray ionization technique,[69] which has been the recent focus of intense investigation mainly in the area of high molecular weight biomolecules, where it has proven wildly successful. This method has the capability of generating multiply-charged metal-containing complexes essentially directly from solution. Given that the second ionization energy of a metal is generally higher than the ionization energy of most organic molecules, an initial prediction might be that simple charge transfer would dominate the reactivity. While charge transfer is significant and sometimes the exclusive process, however, it is by no means the only chemistry observed.

Tonkyn and Weisshaar opened the door to this area by reporting that Ti^{2+}, generated by laser desorption, undergoes clustering reactions with methane and hydride abstraction from ethane in a flowing afterglow.[70] Simple charge transfer, however, was the predominant reaction with propane. This encouraged us to investigate the reactivity of some other doubly-charged early transition metal ions under the low-pressure conditions $(10^{-6}-10^{-9}$ Torr) in the FTICR.[71] Early transition metals have relatively low second ionization energies, with La, at 11.4 eV, being the lowest.

La^{2+}, like La^+, is unreactive with methane.[72] The absence of charge transfer is consistent with the higher ionization energy of CH_4 of 12.6 eV. Interestingly, La^{2+} is also unreactive with ethane, whereas La^+ reacts by dehydrogenation to form $LaC_2H_4^+$.[73] La^{2+} does react with propane by dehydrogenation and demethanation, reactions 14 and 15, respectively.

$$La^{2+} + C_3H_8 \longrightarrow LaC_3H_6^{2+} + H_2 \quad (14)$$
$$\longrightarrow LaC_2H_4^{2+} + CH_4 \quad (15)$$
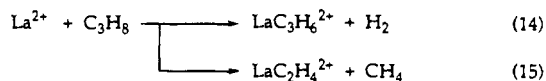
$LaC_2H_4^{2+}$, generated in reaction 15, reacts further with propane by ligand-displacement reaction 16 to form $LaC_3H_8^{2+}$. This surprising result indicates that C_3H_8 is bound more strongly to La^{2+} than ethylene and is a consequence of the mainly electrostatic bonding of La^{2+} in these complexes.[74] The reactions

$$LaC_2H_4^{2+} + C_3H_8 \rightarrow LaC_3H_8^{2+} + C_2H_4 \quad (16)$$
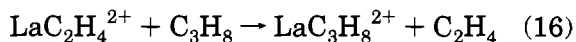
of La^{2+} and for comparison its congener, Y^{2+},[75] with butane are given in reactions 17–24. The absence of charge transfer reaction 23 for La^{2+} is at first surprising, since butane has an ionization energy of 10.53 ± 0.1 eV, well below that of the second ionization energy of La. Even though the second ionization energy of yttrium at 12.4 eV is 2 eV above that of butane, still only 10% charge transfer is observed.

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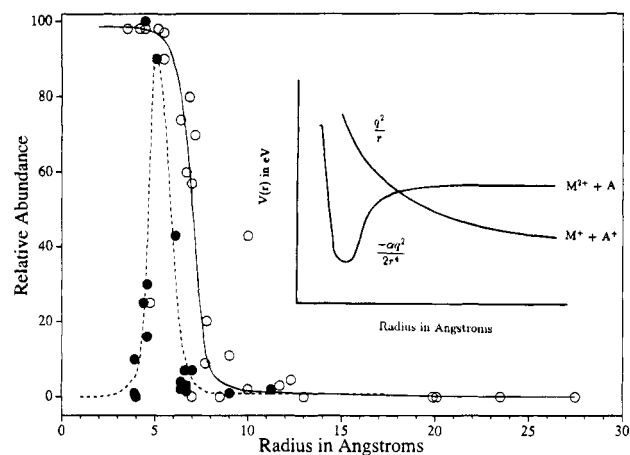
Figure 5. (inset) Potential energy curves for M^{2+} reacting with a molecule A by a charge transfer process. (O) Relationship between the relative abundance of charge transfer and the critical transfer distance. (●) Relationship between the relative abundance of hydride transfer and the critical transfer distance. The lines are an aid to visualizing the trend and are not a fit to the data. The data are taken from refs 71 and 75.

		La	Y	
$M^{2+} + C_4H_{10} \longrightarrow$	$MC_4H_8^{2+} + H_2$	38	3	(17)
	$MC_4H_6^{2+} + 2H_2$	11	11	(18)
	$MC_2H_4^{2+} + C_2H_6$	34	34	(19)
	$MCH_3^+ + C_3H_7^+$	8	28	(20)
	$MH^+ + C_4H_9^+$	3	3	(21)
	$MC_3H_6^{2+} + CH_4$	6	6	(22)
	$M^+ + C_4H_{10}^+$	-	10	(23)
	$M_2H_5^+ + C_2H_5^+$	-	5	(24)

This behavior can be explained by a simple curve-crossing model based on Landau–Zener considerations.[70] Figure 5 (inset) depicts this model as a two-dimensional potential energy diagram in which the reactants, M^{2+} + organic, enter on an attractive ion–induced-dipole curve. This curve is described by $-\alpha q^2/2r^4$, where α is the polarizability of the neutral, q is the ionic charge, and r is the distance between the reactants as they approach each other. The two singly-charged product ions, resulting from either transfer of negative charge from the neutral to the dication (e.g., electron, hydride, methide, etc.) or by transfer of positive charge from the dication to the neutral (e.g., proton transfer, etc.), exit on a repulsive curve described by q^2/r. At infinite distance, the energy difference between the two curves is given by the exothermicity of the reaction channel under consideration. Also, whether the products are in their ground or excited states clearly must be taken into account by this energy difference. The intersection between the reactant and product curves provides an estimate of the critical distance at which it is energetically feasible for a charge-splitting reaction to occur.

The remarkable success of this simple curve-crossing model is evident from the data in Figure 5, which plots percentage of charge splitting versus critical distance. Plotting the data versus reaction exothermicity shows similar trends and indicates that a charge-splitting reaction must be on the order of 1.5 eV exothermic before it will be observed. The data strongly suggest that electron and hydride transfer are both "physical processes" controlled by the positions of the curve-crossing points, which in turn are con-

trolled only by the exothermicities of the two channels. The more exothermic the reaction, the closer the critical distance and the greater the likelihood for the reaction to occur. Alternatively, less exothermic charge-splitting reactions will allow more "chemical" processes to become competitive, such as those for La^{2+} in reactions 14–24. Note that a relatively narrow range for critical distances is observed for hydride transfer in Figure 5. If the distance is too great, hydride transfer is not possible, while if the distance is too close, electron transfer dominates.

Additional studies in our laboratory have focused on characterizing the chemistry of a variety of M^{2+} species (M = Y, Zr, Nb, La, and Ta) with simple alkanes,[71,72,75,76] generating and characterizing the long-lived mixed dimer LaFe^{2+},[77] obtaining M^{2+} bond energies for comparison to theory and to bond energies of the singly-charged metal ions,[72,78] and measuring kinetic energy release in charge-transfer reactions to obtain information on energy distribution and formation of internally hot products.[79]

Returning to the original question about studying ions observed in solution such as Fe^{2+} and Fe^{3+}, the curve-crossing model predicts charge transfer for these ions in most cases. The method of electrospray ionization, however, opens up an exciting new realm of possibilities by providing a method of transferring preexisting ions from solution into the gas phase. Of particular relevance here is a study by Kebarle and co-workers[80] in which they generated a series of hydrates and other ligand complexes of M^{2+} (M = Mg, Cu, Sr, Ba, Mn, Fe, Co, Ni, Zn) and obtained information on successive H$_2$O attachment energies by equilibrium and CID measurements. As stated by the authors, the results obtained by the electrospray method "indicates the dawning of a new era of gas-phase metal ion M^{2+} studies."

Future Directions

There is no sign that the development of new mass spectrometric methods is slowing down. If anything, it is speeding up! With regard to FTICR instrumentation, since the key components are the computer and the magnet (the vacuum system can be relatively simple), and the technology of both of these is advancing rapidly, the future of FTICR looks very bright indeed. For example, an FTICR having a 20 T magnet is currently under construction at Florida State University.[81] In the area of chemical ionization, the surface has just been scratched with regard to taking advantage of the different reactivities of bare metal ions for addressing certain problems of structure and functionality. One can envision using ligated metal ions or ions from organometallic complexes which, for example, may be known (from solution studies) to bind specifically to certain organic or bioorganic molecules,

to look for active sites or for performing sequencing. While the data base on the thermochemistry and reactivity of ML$^+$ species continues to grow, exploration into the effect of having a second, a third, and more ligands is beginning to emerge.[82] These studies, together with studies on solvated metal containing ions,[80,83] will start to bring the gas-phase results into greater view of the condensed-phase organometallic chemist. Along these lines, the electrospray ionization method, especially used in conjunction with FTICR, will open new doors for studying organometallic ion chemistry of "greater relevance" to the general scientific community. Even in the absence of electrospray, these studies have begun to appear. For example, Richardson and co-workers[84] have done extensive studies on the electron-transfer kinetics and thermochemistry of various organometallic complexes, and Dearden and Brodbelt and their co-workers have reported on host–guest and macrocyclic chemistry.[85] In addition, Schwarz and co-workers[2a] have done extensive studies on the gas-phase analogy to remote functionalization using elegant deuterium labeling experiments. The enormous area of cluster chemistry, which was only alluded to, continues to be another promising frontier for ion chemists. Mass spectrometry permits the detailed study of the effect of size and composition on reactivity.[3] Characterizing these effects will aid greatly in the understanding of heterogeneous catalysis and surface chemistry. Lastly, with the discovery of C$_{60}$, one must take seriously the possibility that a particularly intense peak in a mass spectrum may arise from a new, useful, and isolatable material. The recent discovery by Castleman and co-workers[86] of metallocarbohedrenes, M$_8$C$_{12}$ species, as intense peaks coming from a supersonic metal cluster source seeded with ~1% CH$_4$ could be the next example. What are the chemistries of these species, are they stable in air, and can they be synthesized in macroscopic amounts? We have recently interfaced a Smalley-type supersonic source to our FTMS to look at metal cluster ion chemistry and have begun seeding it with various gases. From now on, we will reclassify "crud" in the source not as annoyance, but as a novel research opportunity!

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