in different sublattices have different canting angles. Since pyridine intercalation proceeds with loss of some Mn^{2+} ions from the host lattice, it is possible that the spins of the Mn^{2+} ions neighboring these vacancies may show a different canting angle (either due to the single ion anisotropy DS_z^2 or antisymmetric exchange $d_{ij}{\cdot}S_i{\times}S_j$) from those ions which are further away from the defect. This may be a possible mechanism for the observation of nearly isotropic weak ferromagnetism. This was confirmed by the angular and temperature variation of the EPR spectra of single crystals of pyridine-intercalated $MnPS_3$ which will be published later.[33]

In hindsight, it is not surprising why the intercalation of pyridine in $MnPS_3$ and the transition metal dichalcogenides proceeds by such different mechanisms. The MPS_3 (M = Mn, Fe, Ni, etc.) are ionic and are best viewed as salts of the thiophosphate anion with the metal–sulfur bond length being reasonably approximated by the sum of the ionic radii.[7] The "d bands" are narrow and the materials are Mott insulators. In contrast, the transition metal dichalcogenides like TaS_2 are more covalent with d electrons delocalized, and the d band widths are large and consequently can easily accommodate an extra electron from the guest species. In $MnPS_3$, however, this would lead to highly localized electron densities (Mn^{1+}) at some centers. Since the Mn^{1+} state is unstable, the above mechanism is unlikely. On the other hand, $MnPS_3$ being ionic, the Mn–S linkages are weak so that the lattice energy required for the removal of a Mn^{2+} ion during an ion exchange is easily compensated by the electrostatic host–guest interactions as well as the solvation energy of the exchanged Mn^{2+} ion.

Metal-Induced Valence Isomerizations: Gas-Phase Reactions of Iron(I) and Copper(I) with Quadricyclane and Norbornadiene

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Abstract: Metal-promoted valence isomerizations and cycloreversions occur in the gas phase for adducts of norbornadiene (NBD) and quadricyclane (Q) with either Fe(I) or Cu(I). The collisionally activated decomposition (CAD) spectra of the adducts of NBD and Q with each metal indicate that the complexes possess identical structures, although the structures that are formed with Fe(I) are different from those with Cu(I). Both Cu(I) and Fe(I) cause the valence isomerization of Q to NBD. The metal ion then induces a retro Diels–Alder reaction of NBD to form a $(C_5H_6)M^+(C_2H_2)$ complex. Only the Fe(I) complexes react further to generate a $(C_5H_5)(H)Fe^+(C_2H_2)$ species. Structures of the adducts of toluene (T) and cycloheptatriene (CHT) with each metal are shown to be similar but non-interconverting with those of NBD and Q. Fourier transform mass spectrometry (FTMS) data provide additional support for the structural assignments. Experimental rate constants for the reactions are nearly equal to each other and to the collision rate constants for each system.

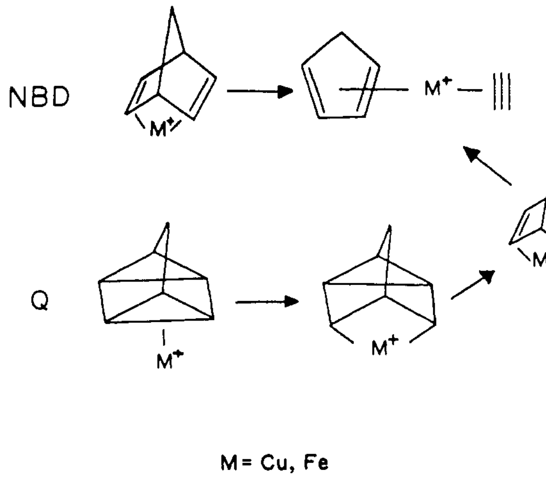
Introduction

The subject of gas-phase transition metal ion reactions with organic molecules has been a focus of numerous investigations in recent years.[1] Metal ion bonding energetics are one area of intense study;[2] however, much of the current effort in the field is concerned with the clarification of mechanisms of reactions such as oxidative addition and remote functionalization.[3] Some evidence for metal ion-induced retro Diels–Alder reactions[4] and other interesting condensations[5] was also revealed by mechanism studies. Little work, however, has been done with gas-phase metal-promoted isomerizations.[6]

There are, to our knowledge, no reported efforts to understand metal-ion-induced valence isomerizations in the gas phase although there are some examples reported for two-phase and condensed-phase systems. Hamilton et al.[7] reported the valence rearrangement of gas-phase Binor-S, a norbornadiene dimer, on a solid platinum surface. Greenberg and Leibman[8] as well as Bishop[9] provide numerous examples of the ability of transition metals in solution either to induce valence isomerizations of kinetically stable strained cyclic molecules or to stabilize transitory species.

We present in this paper the results of an inquiry into the ability of Fe^+ and Cu^+ to initiate valence isomerizations of quadricyclane[10] (Q) and norbornadiene[11] (NBD) in the gas phase. Both are strained C_7H_8 isomers and have been considered for possible chemical energy storage systems.[12] Isomerization of NBD to Q stores energy in Q. That energy is released upon reversion of Q to NBD.

Scheme I



We used two complementary tools to study Fe^+ and Cu^+ adducts of C_7H_8 isomers: tandem mass spectrometry (MS/MS)

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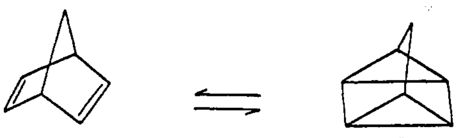
and Fourier transform mass spectrometry (FTMS). MS/MS permits an ion of interest to be formed at high pressure (e.g., 0.1 Torr) and then selected so that collisionally activated decompositions (CADs) can be called upon to provide characteristic information about its structure. FTMS was employed to obtain additional information such as rate constants and ligand-exchange propensities as well as other evidence to support the structure assignments.

Rapid valence isomerization of NBD (**1**) to Q (**2**) occurs photochemically (eq 1) in solution with sensitization by metal carbonyl compounds[13] or by transition metal complexes.[14] Photoisomerization of NBD to Q is efficiently sensitized by both (phosphine)copper(I) halide complexes and CuCl.[15] The reverse process, valence isomerization of Q to NBD, occurs slowly at room temperature[16] and releases approximately 27 kcal/mol of stored energy.[17] Of relevance to this study is the observation that reversion of Q to NBD is catalyzed by $CuCl_2$ in benzene.[18] Catalysis of the isomerization of Q to NBD by other transition metal ions was also demonstrated.[19–22]



1 2 (1)

Scheme II

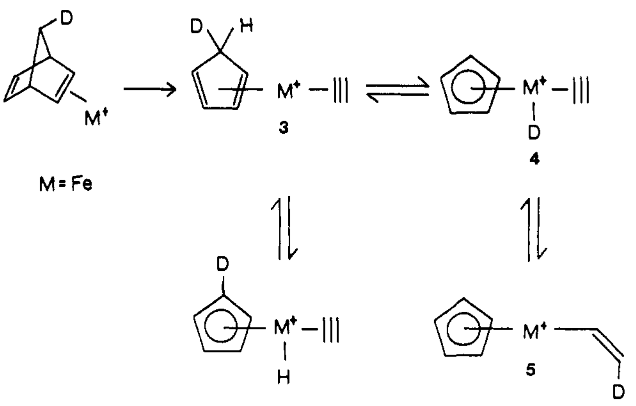


Table I. Calculated and Observed Distributions of Collisionally Activated Loss of Acetylene and Vinyl Groups from Fe(NBD-*7-d*)$^+$

fragment ions		% relative abundance	
m/z	loss	obsd	calcd[a]
123	C_2H_2	58	62
122	C_2HD; C_2H_3	34	32
121	C_2H_2D	8	6

[a] Assuming complete H/D interchange.

Although the valence isomerization of Q to NBD by gas-phase metal ions has not been considered previously, the reactivity of NBD with Rh$^+$ and Co$^+$[4] as well as with CuFe$^+$[23] was investigated by Freiser and co-workers. Quadricyclane was not included in these studies. A transition metal-mediated cycloreversion of NBD to eliminate C_2H_2 and form $M(C_5H_6)^+$, however, was demonstrated.

An additional goal of this study is to gain a better understanding of the specific reactivities of Fe$^+$ and Cu$^+$. Both metal ions activate allylic carbon–carbon bonds of alkenes,[1a] but they exhibit differing reactivities with nitriles.[24] The reactivity of Cu$^+$ with alkenes is considered by some to be surprising because its ground electronic configuration, $3d^{10}$, should be stable and unreactive via the oxidative additions that are the hallmark of Fe$^+$ reactivity.[1b] Furthermore, the higher energy needed to promote two electrons to the 4s state, which is thought to be needed to induce oxidative addition chemistry, is considerably lower for Fe$^+$ than for Cu$^+$,[25,26] endowing Fe$^+$ with a rich reactivity toward organic molecules.[27]

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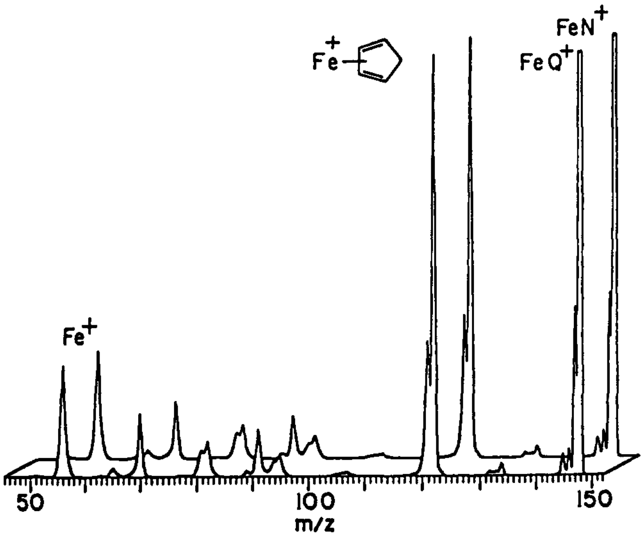

Figure 1. CAD mass spectra of FeQ^+ and $FeNBD^+$.

Gas-phase Cu^+ is sometimes less reactive than are metal ions that oxidatively add to organic compounds.[28-31] Copper(I), however, does react similarly to Co^+ and Ni^+ with alkanes in experiments in which translational energy is added to overcome endothermicity,[32] and when sputtered into the gas phase, it inserts into C–C and C–H bonds of alkanes.[33] Although dissociative attachment explains the reactivity of Cu^+ with heteroatom-containing organics,[34-36] oxidative addition also appears to occur.[37,38]

Results and Discussion

Gas-phase Fe^+ or Cu^+ ions react with C_7H_8 isomers in the source of the tandem mass spectrometer or in the cell of an FT mass spectrometer to form $M(C_7H_8)^+$ adducts. The results of the experiments with these adducts are divided for discussion purposes into two sections according to the identity of the metal ion.

Table II. Calculated and Observed Distribution of Collisionally Activated Loss of Acetylene and Vinyl Groups from $Fe(C_7H_{8-x}D_x)^+$

complex m/z	C_5D_6–Fe^+ – C_2H_2 obsd	C_5D_6–Fe^+ – C_2H_2 calcd[a]	C_5H_6–Fe^+ – C_2D_2 obsd	C_5H_6–Fe^+ – C_2D_2 calcd[a]
128	6	2		
127	30	28		
126	47	39		
125	13	18		
124	4	12	40	36
123			31	40
122			16	20
121			13	4

[a] Assuming complete H/D interchange.

Table III. Fragment Ions Observed in the CAD Mass Spectra of $FeCHT^+$ and FeT^+

fragment ions m/z	fragment ions loss	% relative abundance $FeCHT^+$	% relative abundance FeT^+
147	$H^•$	100	28
146	H_2	7	
145	H_2, $H^•$	3	3
134	CH_2	19	
133	$^•CH_3$	7	11
132	CH_4		7
122	C_2H_2	58	
121	$^•C_2H_3$	12	4
107	$^•C_3H_5$	4	5
95	$^•C_4H_5$	8	10
91	$^•FeH$	62	62
81	$^•C_5H_7$	13	17
70	C_7H_6	91	
65	FeC_2H_3	8	7
56	C_7H_8	54	100

Fe^+ Adducts. The CAD spectra of $FeNBD^+$ and FeQ^+ are identical, as illustrated in Figure 1. For both adducts, the predominant fragment is an ion of m/z 122, $Fe(C_5H_6)^+$, formed by a loss of acetylene. Freiser and co-workers observed that C_2H_2 loss also occurs from adducts of NBD with Rh^+ and Co^+,[23] as well as with $CuFe^+$.[24]

To probe further the structure of the adduct, the CAD spectrum of $Fe(C_5H_6)^+$, formed in a gas-phase reaction between Fe^+ and freshly cracked cyclopentadiene, was taken and found to be nearly identical to that of $Fe(C_5H_6)^+$, obtained from FeQ^+ by using two stages of collisional activation (MS/MS/MS). The latter experiment permits activation of the $Fe(C_5H_6)^+$ ion formed without question from $Fe(C_7H_8)^+$. Ions of m/z 121, 95, and 56 are produced by the losses of H, C_2H_3, and C_5H_6, respectively. Thus, the ions of m/z 122 formed in the collisionally activated decompositions of $FeNBD^+$ and FeQ^+ have the same structure as that of Fe(cyclopentadiene)$^+$.

The CAD spectra of the two $Fe(C_7H_8)^+$ ions indicate that FeQ^+ and $FeNBD^+$ have identical structures. That structure may involve a complex of Fe^+, cyclopentadiene, and acetylene, formed by a retro Diels–Alder (RDA) reaction and capable of decomposing to $Fe(C_5H_6)^+$. A retro Diels–Alder reaction was also proposed for the interaction of Co^+ and NBD.[23]

Formation of $Fe(C_5H_6)^+$ from FeQ^+ is apparently preceded by a metal-assisted valence isomerization of Q to NBD, possibly beginning with Fe^+ associating with one of the cyclopropane rings of quadricyclane. Hankinson and Allison[39] suggested that the electrostatic interaction of a metal ion with an organic species in a complexation step strongly influences the final product distribution. Cyclopropane ring functionalities possess alkene-like character and provide an interaction site for transition metals.[7] Furthermore, cyclopropane C–C bonds are weak, owing to ring strain, and thus more susceptible to attack than other sites on Q.[40] Either the initial anchoring interaction or an oxidative addition of Fe to a C–C bond, as shown in Scheme I, causes the valence isomerization to NBD. After the valence isomerization, rearrangement via a metal-assisted RDA reaction converts $FeNBD^+$ to a $(C_5H_6)Fe^+(C_2H_2)$ complex. Collisional activation of this

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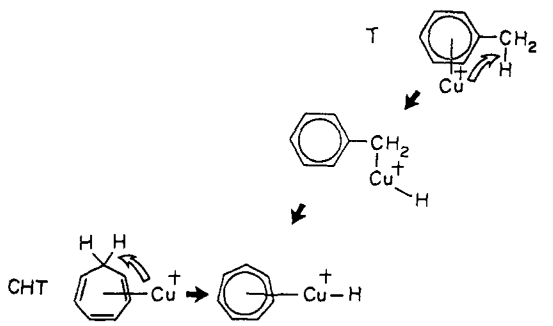
Scheme III



species produces an abundant $FeC_5H_6^+$ fragment that has the structure of Fe(cyclopentadiene)$^+$, a result that is difficult to explain without invoking valence isomerization.

Jacobson and Freiser[41] reported that six H/D exchanges occur between Fe(cyclopentadiene)$^+$ and C_2D_4. These results are evidence that Fe(cyclopentadiene)$^+$ exists in part as a hydrido–cyclopentadienyl complex. Upon high-energy collisional activation (CA) of the $Fe(C_5H_6)^+$ precursor ion, formed in a CI-FAB source, an abundant $Fe(C_5H_5)^+$ ion is produced, in accord with the proposed hydrido–cyclopentadienyl structure. A similar result was also obtained upon CAD of Fe(cyclopentadiene)$^+$ formed in a CI source.[3b]

The CAD spectrum of Fe(NBD-7-*d*)$^+$ was obtained to elucidate further the structure of the FeQ^+ and $FeNBD^+$ adducts and their $Fe(C_5H_6)^+$ fragments. Interchange of H and D must occur because losses of both C_2H_2 and C_2HD occur (a mechanism for H/D interchange is depicted in Scheme II). The observed spectrum and the calculated statistical distribution for complete exchange are in good agreement (Table I). We, therefore, conclude that H/D transfer is rapid and complete, the intermediate, **4**, is stable and long-lived, and the rate-determining step of the reaction is not H/D transfer.

Additional experimental evidence supports the proposed formation of the hydrido–cyclopentadienyl complex, **4**. Complexes of (cyclopentadiene)Fe^+(acetylene) with one ligand fully deuterated were formed in the CI source. The distribution of products (Table II) is similar to the calculated statistical distribution that pertains to complete H/D exchange. The small deviation suggests that interchange is preempted by fragmentation.

In contrast to the CAD spectra of the Q and NBD adducts, those of Fe^+ with toluene (T) and cycloheptatriene (CHT) are unique (Table III). Upon complexation with Fe^+, T rearranges less than does CHT. The reactions of CHT and T with Fe^+ are similar to those reported for C_7H_8 isomers with Co^+.[18] The predominant structure for both adducts appears to be a $(C_7H_7)Fe^+(H)$ species formed by means of the steps outlined in Scheme III for Cu^+. These results underscore the potential efficacy of metal ion chemical ionization in structural studies.[42]

FTMS. We used FTMS to investigate both the formation and structure of the adducts of NBD and Q with Fe^+. Structural information is derived from the appearance of the mass spectra of adduct fragments and from the results of ligand-exchange experiments.

Both NBD and Q react with Fe^+ in the FT mass spectrometer to give detectable adducts, a situation that often does not apply to organic ion–molecule reactions. A fraction of the adducts further decompose to give a spectrum of product ions that is similar to the CAD spectra discussed above. In general, CAD and FT mass spectra are often similar, as was discussed by Eller and Schwarz.[43] Loss of C_2H_2 from the adduct is the most facile decomposition. Addition of C_7H_8 to each adduct to give $Fe(C_7H_8)_2^+$ is also observed. These results are consistent with those expected from the proposed adduct structure.

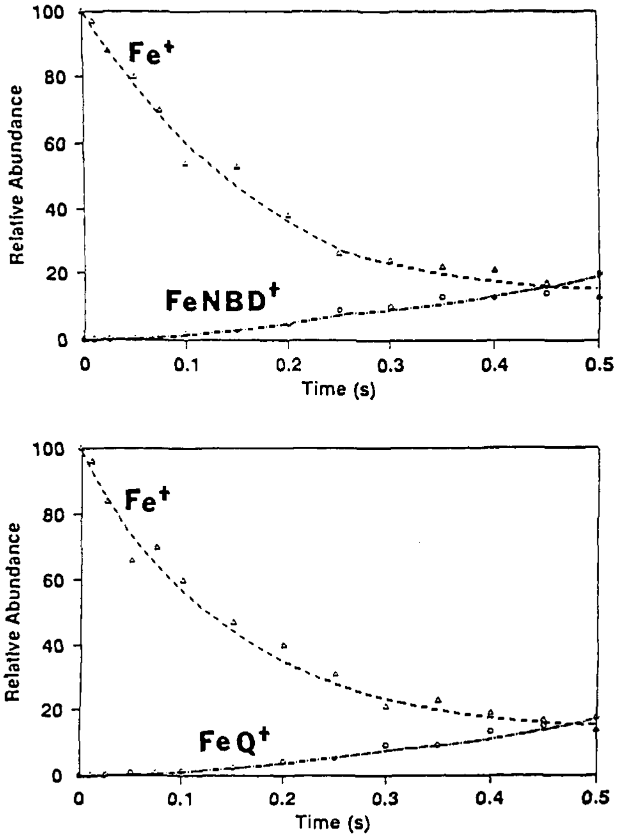


Figure 2. Time dependence of signal intensity for $FeNBD^+$ and FeQ^+ in the FTMS experiment.

Ligand-exchange experiments with C_2D_2 were performed to probe further the structure of the adducts. If a significant fraction of the adducts is $(C_5H_6)Fe^+(C_2H_2)$, exchange of C_2H_2 with C_2D_2 would be expected. The adduct from each system was isolated in the FTMS cell by ejection of ions above and below it in mass. Deuterated acetylene was then admitted to the cell via a pulsed valve, and ligand exchange of bound C_2H_2 with free C_2D_2 was observed. But because the processes depicted in Scheme II are possible, more than simple exchange of ligands occurs. Exchange of H/D takes place to move deuteriums to the C_5H_6 portion of the adduct; in fact, five deuterium atoms are taken up by both $FeNBD^+$ and FeQ^+. This observation points to hydrido transfer to the metal center from both unsaturated ligands, as presented in Scheme II. Additional ligand exchange leads to even more uptake of deuterium by the adduct. The appearance of the exchange products as well as the occurrence of H/D transfer is strong verification that the adduct exists as both $(C_5H_6)Fe^+(C_2H_2)$ and $(C_5H_5)(H)Fe^+(C_2H_2)$.

FTMS data also provide insight into the reaction kinetics. The intensity of the Fe^+ signal decays exponentially as a function of time for both the $FeNBD^+$ and FeQ^+ systems (see Figure 2). Experimental reaction rate constants were obtained from the pseudo-first-order rate constants and the ion density in the FTMS cell. The ion density was calculated by measuring the pseudo-first-order rate constant of the well-characterized reference reaction of toluene reacting with the $C_7H_7^+$, which is formed by loss of H from toluene.[63] Assuming that toluene, NBD, and Q have similar ionization cross sections and ionization gauge responses, we calculated the first-order rate constants for the $FeNBD^+$ and FeQ^+ systems.

Comparison of the experimentally determined values with the theoretical Langevin collision rate constants[44] indicates that both reactions occur more slowly than theory predicts, but the factor is only ca. 0.5 (see Table IV). The polarizabilities of NBD and Q (1.13×10^{-23} and 1.07×10^{-23} cm^3, respectively) were estimated

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Table IV. Rate Constants for Fe^+ and Cu^+ Reacting with NBD and Q

reaction	k,[a] cm^3/molecule	k_L,[b] cm^3/molecule
$\mathrm{C_7H_7^+ + C_7H_8}$	1.6×10^{-10}	
$\mathrm{Fe^+}$ + NBD	8×10^{-10}	1.34×10^{-9}
$\mathrm{Fe^+}$ + Q	6×10^{-10}	1.30×10^{-9}
$\mathrm{Cu^+}$ + NBD	1×10^{-9}	1.29×10^{-9}
$\mathrm{Cu^+}$ + Q	7×10^{-10}	1.25×10^{-9}

[a] The value for the $\mathrm{C_7H_7^+ + C_7H_8}$ reaction is taken from ref 64. The remaining values are calculated from $k = k'n$, as described in the text, where n = ion density. [b] The Langevin rate constants are calculated in cgs units.

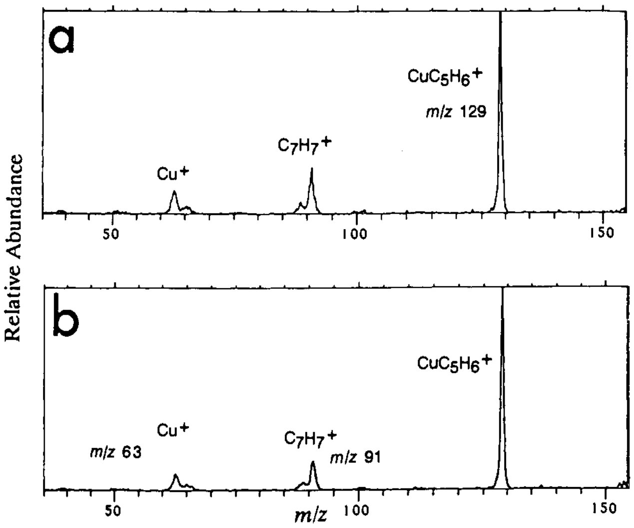

Figure 3. CAD mass spectra of (a) $\mathrm{CuQ^+}$ and (b) $\mathrm{CuNBD^+}$.

according to the method of Le Fevre.[45] The experimental rate constant is often larger than the theoretical Langevin rate constant for a reaction in which a reactant has a permanent dipole. Theoretical rate constants of reaction for such species can be calculated by using ADO theory.[46] The ADO rate constants in this instance are, however, essentially equal to the Langevin rate constants because both NBD and Q have relatively small permanent dipole moments (0.05[47] and 0.019 D,[48] respectively).

$\mathrm{Cu^+}$ Adducts. The CAD spectra of $\mathrm{CuQ^+}$ and $\mathrm{CuNBD^+}$ are identical to each other, as illustrated in Figure 3, but the adducts fragment somewhat differently than do the $\mathrm{Fe^+}$ adducts. Both $\mathrm{Cu^+}$ adducts, like their $\mathrm{Fe^+}$ counterparts, lose acetylene readily to form an ion of m/z 129, $\mathrm{Cu(C_5H_6)^+}$. Other ions that are not produced from the $\mathrm{Fe^+}$ adducts, however, are also observed. Significantly, the $\mathrm{Cu^+}$ adducts eliminate no detectable $\mathrm{C_2H_3}$, whereas the $\mathrm{Fe^+}$ adducts do.

The CAD spectrum of $\mathrm{Cu(C_5H_6)^+}$, formed in a gas-phase reaction between $\mathrm{Cu^+}$ and freshly cracked cyclopentadiene, is nearly identical that of $\mathrm{Cu(C_5H_6)^+}$ formed unambiguously from the $\mathrm{CuQ^+}$ adduct as determined by MS/MS/MS. We conclude that $\mathrm{Cu(C_5H_6)^+}$ produced from $\mathrm{CuQ^+}$ has the same structure as Cu(cyclopentadiene)$^+$ and, thus, the stable adduct species structure is that of a cyclopentadiene–acetylene complex.

The ligand-exchange results and the appearance of the CAD mass spectra serve to demonstrate that $\mathrm{Cu^+}$ initially interacts with Q to induce first valence isomerization of Q to NBD and then cycloreversion, just as does $\mathrm{Fe^+}$. The interaction may be simple complexation or oxidative addition. If oxidative addition occurs, $\mathrm{Cu^+}$ is likely to interact with an olefin or with the π-like electron density of a cyclopropane according to the Dewar–Chatt–Duncanson model[49] by donating electron density from the filled d_{xy} orbital into a π^* orbital of the olefin. The olefin then donates electron density from its filled p orbital into the empty $\mathrm{Cu^+}$ 4s orbital.[50] The newly ligated $\mathrm{Cu^+}$ will have a lower promotion energy than that of the bare metal ion because electron density is shifted to the metal ion, allowing $\mathrm{Cu^+}$ to participate in the oxidative addition reaction. Furthermore, the bonds in the organic entity are weakened by the shift in electron density to the metal, and that also facilitates oxidative addition. Georgiadis et al.[32] and Hill et al.[51] recently observed strong $\mathrm{Cu^+}$–alkane interactions and suggested that electron donation from alkanes to the empty $\mathrm{Cu^+}$ 4s orbital does occur.

Table V. Fragment Ions Observed in the CAD Mass Spectra of $\mathrm{CuCHT^+}$ and $\mathrm{CuT^+}$

fragment ions		% relative abundance	
m/z	loss	$\mathrm{CuCHT^+}$	$\mathrm{CuT^+}$
154	$\mathrm{H^\bullet}$	22	100
153	$\mathrm{H_2}$	14	14
152	$\mathrm{H_2, H^\bullet}$	9	1
140	$\mathrm{CH_3}$	2	8
139	$\mathrm{CH_4}$	4	11
129	$\mathrm{C_2H_2}$	16	
128	$\mathrm{C_2H_3}$	10	
127	$\mathrm{C_2H_4}$	6	2
113	$\mathrm{C_3H_6}$	5	4
101	$\mathrm{C_4H_6}$	8	4
91	CuH	100	90
89	$\mathrm{C_5H_6}$	22	12
77	$\mathrm{CuCH_3}$	5	3
65	$\mathrm{CuC_2H_3}$	23	16
51	$\mathrm{CuC_3H_5}$	7	6
39	$\mathrm{CuC_4H_5}$	10	6

It is noteworthy that no hydrogen transfer from the cyclopentadiene ligand to the copper metal and then to the acetylene ligand is apparent. A likely explanation involves the relative stability of the complexes, resulting from the number of electrons surrounding the metal center. The $\mathrm{(C_5H_6)Cu(C_2H_2)^+}$ adduct is a relatively stable 16-electron complex whereas the corresponding $\mathrm{Fe^+}$ adduct has 13 electrons surrounding the metal center. Transfer of a hydride increases the electron count around the iron center to 15.

Other ionic fragments of $\mathrm{Cu(NBD\text{-}7\text{-}}d)^+$, including $\mathrm{C_7H_6D^+}$, $\mathrm{CuC_2H_2^+}$, and $\mathrm{Cu^+}$, are produced upon CA. The proposed retro Diels–Alder mechanism is also consistent with the formation of the $\mathrm{CuC_2H_2^+}$ fragment. The unlabeled counterpart of $\mathrm{C_7H_6D^+}$, namely $\mathrm{C_7H_7^+}$, is observed in low abundance. Hydride abstraction, also observed for the $\mathrm{Fe^+}$ system, yields the $\mathrm{C_7H_6D^+}$ species. The low abundance of $\mathrm{C_7H_7^+}$ suggests that all sites are equivalent for hydride (or correspondingly, deuteride) abstraction.

The CAD mass spectra of $\mathrm{CuT^+}$ and $\mathrm{CuCHT^+}$ and similar (Table V). Loss of $\mathrm{C_2H_2}$ from both $\mathrm{CuCHT^+}$ and $\mathrm{CuT^+}$ is minor, whereas the ion of m/z 91 ($\mathrm{C_7H_7^+}$) is most abundant. $\mathrm{CuCHT^+}$ and $\mathrm{CuT^+}$ achieve a similar structure, but one that is distinct from that reached for $\mathrm{CuNBD^+}$ and $\mathrm{CuQ^+}$. The likely structure for the $\mathrm{CuCHT^+}$ and $\mathrm{CuT^+}$ adducts is the $\mathrm{(C_7H_7)Cu^+(H)}$ complex depicted in Scheme III. Neither $\mathrm{Fe^+}$ nor $\mathrm{Cu^+}$ causes interconversion of T or CHT to NBD or Q.

One may question whether the reactivity of $\mathrm{Cu^+}$ is due to an excited-state species. To answer this inquiry, we performed charge-stripping experiments to measure the second ionization potential of $\mathrm{Cu^+}$. Only one product peak was observed in the charge-stripping spectrum. We experimentally obtained a second ionization potential of 20.4 ± 0.6 eV for $\mathrm{Cu^+}$, a value which compares well with the literature value of 20.29 eV.[52] The

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presence of an excited Cu^+ precursor would have been indicated by an additional charge-stripping peak at a lower energy than that for ground-state Cu^+. These results do not preclude a small contribution (<10%) of excited-state ions, however. Experiments by Elkind and Armentrout[53] show that ground-state Cu^+, generated by surface ionization, has a larger reactive cross section for reaction with simple gases such as H_2, D_2, and HD than does excited-state Cu^+. The authors suggested that electronic configuration, rather than electronic state, determines reactivity. Similar conclusions were reached by Huang et al.[54] in a study of metal cation reactions with alcohols.

FTMS. FTMS experiments with the $Cu(C_7H_8)^+$ systems provide additional evidence for the metal-assisted valence isomerization of Q to NBD. Both $CuNBD^+$ and CuQ^+ adducts are observed. The products of the reactions of Cu^+ with NBD and Q and their relative abundances are identical. All ions observed in the CAD spectra are apparent in the FT mass spectra. Addition of C_7H_8 to the adduct now occurs to only a small extent.

Ligand exchanges with both adducts are consistent with the assigned structures. In an experiment similar to that used for ligand exchange with the Fe^+ adducts, C_2D_2 was pulsed into the cell after isolation of both the ^{62}Cu and ^{64}Cu isotopes of the Cu^+ adduct. Complete exchange of C_2H_2 by C_2D_2 was observed for both copper-isotope-containing species, but no H/D exchange was detected. This evidence gives strong support to the proposal that the stable structure of the adduct is $(C_5H_5)Cu^+(C_2H_2)$. In contrast to the Fe^+ systems, the Cu^+ adducts produce simple spectra, pointing to reduced reactivity (greater selectivity) of Cu^+. A similar result pertains to Ni(cyclopentadiene).[55]

Experimental rate constants were also obtained for the Cu^+ systems. As for the Fe^+ systems, the rate constants are nearly equal to each other. Interestingly, Cu^+ reacts with NBD and Q completely and slightly more efficiently than does Fe^+. A comparison of the Langevin rate constants given in Table IV with those determined experimentally indicates that the reactions of Cu^+ with NBD and Q occur at factors of ca. 0.8 and 0.6 times the theoretical collision rate, respectively. As with the Fe^+ systems, the ADO rate constants for the reactions of Cu^+ with NBD and Q are nearly identical to the Langevin rate constants.

Conclusions

Both Fe^+ and Cu^+ catalyze the valence isomerization of Q to NBD after initially interacting with the cyclopropane rings of Q. Both metal ions are sufficiently reactive to cause the NBD ligand to cyclorevert in a subsequent rearrangement to give cyclopentadiene–acetylene complexes. The principal evidence for this is the ligand-exchange experiment, which is particularly clear for the $(C_5H_6)Cu^+(C_2H_2)$ species because there is no H/D interchange in the adduct. H/D interchange takes place in Fe^+ adducts via a hydrido–cyclopentadienyl species, which also leads to the loss of C_2H_3, an elimination that is not seen for Cu^+ adducts. The low electron count around the Fe^+ center encourages the hydrido formation, but the Cu^+ adducts are stable, even-electron ions that do not demand the additional electron density provided by the hydrido entity.

The ligand-exchange experiments also reveal the timetable for the cycloreversion. Both Cu^+ and Fe^+ induce the retro Diels–Alder reactions by virtue of their complexation with the organic species, which, for NBD and Q, occurs at nearly the collision rate. No collisional or other activation is needed.

Further study of the energy uptake upon collisional activation and the kinetic energy release distribution upon decomposition of these highly interesting systems is underway.

Experimental Section

MS/MS. All CAD mass spectra were obtained with a Kratos MS-50 triple analyzer (TA) mass spectrometer of EBE geometry,[56] where E refers to the electric sector and B to the magnetic sector. Metal ion–molecule adducts were formed either in a high pressure chemical ionization (CI) source or in a FAB source that was custom-modified to achieve CI conditions (CI-FAB).[57] Copper ions were generated by electron ionization of cupric acetylacetonate in the CI source or by sputtering Cu^+ either from solid $CuCl_2$ applied in solution to the probe tip or from the copper probe tip itself. Iron ions were formed upon electron ionization of $Fe(CO)_5$ introduced into the ion source with a specially designed gas/liquids probe[3b] or by sputtering Fe^+ either from solid Fe_2SO_4 applied in solution to the probe tip or from an iron probe tip itself. The CI source was operated at 280-eV ionization energy with a total emission current of 500 μA. The saddle field FAB gun used in conjunction with the CI-FAB source was operated at 1 mA and 6 kV. The ion-accelerating voltage was 8 kV. The selected ion beam was collisionally activated by introducing helium collision gas to a pressure sufficient to cause 30% suppression of the ion beam. Most ions undergo one collision at this level of activation.[58]

FTMS. FTMS data were obtained with a custom-built FT mass spectrometer[59] interfaced to a Nicolet 2000 data system. The FT mass spectrometer was operated at a magnetic induction of 1.2 T, and a 5.08-cm cubic cell was used. Copper or iron ions were produced by laser desorption[60] from a metal probe tip by using either the fundamental wavelength or the fourth harmonic (266 nm) of a Nd-YAG DCR-2 laser (Quanta Ray, Mt. View, CA) equipped with a Model HG-2 harmonic generator. The laser beam was filtered through a Schott UG II filter when the fourth harmonic was used and not filtered when the fundamental wavelength was employed. Each neutral hydrocarbon was introduced into the cell via Varian leak valves to a pressure of 2×10^{-7} Torr (uncorrected), as measured by a Bayard-Alpert ionization gauge situated near the cell. A computer-triggered pulsed valve[61] was used to admit C_2D_2 for the ligand-exchange experiments. A trap voltage of 1 V was used to minimize ion evaporation.[62]

The reaction kinetics were monitored by varying the reaction time prior to the detection pulse. For these experiments, the density of the neutral molecule was determined from the well-characterized reaction of $C_7H_7^+$ with toluene.[63] A filament producing 30-eV electrons over a 3-ms beam time was employed. The density of toluene at an ionization gauge reading of 1.5×10^{-6} Torr was calculated to be 6.7×10^9 molecules/cm^3. Rate constants for the reactions of metal ions with Q and NBD were calculated by assuming Q, NBD, and T have the same ionization cross section and, thus, the same ionization gauge response.

Reagents. Most reagents were purchased and used without further purification other than submitting them to multiple freeze–pump–thaw cycles. NBD, Q, T, CHT, and $Fe(CO)_5$ were purchased from Aldrich Chemical Co. (Milwaukee, WI). Cupric acetylacetonate was purchased from Pfaltz and Bauer, Inc. (Waterbury, CT). Cyclopentadiene was freshly cracked from dicyclopentadiene (Chemical Samples Co., Columbus, OH) by distillation at 35 °C. The NBD-*7-d* was synthesized according to the method of Clarke and Johnson.[64] Deuterated acetylene was formed by dropping D_2O (Aldrich) onto CaC_2 (Aldrich). Hexadeuteriocyclopentadiene was synthesized by deuterioxide-catalyzed exchange in a hexamethylphosphoramide solution.[65]

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