Photodissociation Processes in Transition-Metal Cation Complexes with Cyclooctatetraene

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Transition-metal cation complexes with 1,3,5,7-cyclooctatetraene of the form $M^+(C_8H_8)_{1,2}$ (M = V, Fe, Ni, and Ag) are produced by laser vaporization in a pulsed nozzle cluster source. The clusters are mass-selected and photodissociated using the second and third harmonics of an Nd:YAG laser (532 and 355 nm). The first-row transition-metal complexes undergo retro-cyclotrimerization to produce M^+(benzene). The photodissociation of $V^+(C_8H_8)$ also produces a significant amount of $V^+(C_5H_5)$. This is attributed to the ability of V^+ to donate electron density to stabilize a cyclopentadienyl anion. Dissociation of $Ag^+(C_8H_8)$ exhibits a photoinduced charge-transfer pathway allowing an upper limit of 2.6 eV to be placed on the binding energy in this system. Complexes with two C_8H_8 molecules primarily dissociate by loss of intact C_8H_8 molecules with some fragmentation to $M^+(C_{10}H_{10})$ for M^+ = V and Fe. Fragmentation of these $M^+(C_{10}H_{10})$ species indicates a structure that is not ferrocene-like in nature. Mixed sandwich complexes are produced with both COT and benzene as ligands, and these dissociate by eliminating benzene, indicating that COT is more strongly bound to these transition-metal ions. The results of these experiments shed new insight on the bonding and photochemistry of these organometallic systems.

Introduction

A fascinating variety of unusual organometallic complexes have been produced by new molecular beam cluster studies, including many novel sandwich complexes.[1−18] The condensed phase synthesis of well-known complexes such as ferrocene[19] and dibenzene chromium[20] has over the years prompted extensive work to investigate sandwiches of various ligands in the gas phase. Theoretical and experimental work has investigated new sandwich complexes containing benzene,[1,13] fullerenes,[5,6,13] and polycyclic aromatic hydrocarbons (PAHs).[11−17] Multiple decker sandwiches have been described for transition metal−benzene complexes,[1,6e] metal−PAH complexes,[12] and metal−fullerenes[6] as well as for lanthanide metal−cyclooctatetraene (COT)[6e,18] systems. Photodissociation has been employed to unravel the structures of some of these complexes.[4−5,12−15,21] In the present work, we use photodissociation measurements to investigate new complexes between transition metals and COT.

Sandwich complexes with COT have been produced previously in the condensed phase[22−25] and in the gas phase.[6e,18] Uranocene was discovered in 1968 by Streitwieser and Müller-Westerhoff[22] and is structurally analogous to ferrocene but contains an actinide core of uranium sandwiched between two COT ligands. Also similar to ferrocene, the stability of the structure is attributed to charge transfer from the metal to the ligands.[23−25] COT itself is antiaromatic with eight π electrons, lacking two electrons to satisfy the aromaticity requirement of $4n + 2$ as established by Huckel's rule. Uranium donates two electrons to each ligand creating aromatic COT dianions, which stabilizes the complex.[23−25] On the basis of this same concept, Kaya and co-workers performed gas-phase studies to investigate the possibility of an extended stacking motif of lanthanide metals with COT.[6e,18] The mass spectra observed in their experiments showed a pattern of magic numbers corresponding to $M_n^+(COT)_{n+1}$ (M = Ce, Nd, Eu, Ho, Yb) species, which they assigned to multiple decker sandwiches. Photoelectron spectroscopy of these complexes gave further evidence for these structures.[18] Unfortunately, these studies were limited to the lanthanide metals mentioned above. Transition metal ion−COT complexes have not been investigated, and these species may be equally interesting. Photodissociation experiments allow the stability of such clusters to be tested.

UV and visible photodissociation studies have been performed previously by our group for many metal cation−ligand systems including $M^+(\text{benzene})_n$,[21] $M^+(C_{60})_n$,[5,13] and $M^+(\text{coronene})_n$.[12−15] In many cases, photodissociation occurs by simple ligand elimination in which an intact neutral ligand leaves the cluster and the metal cation or a smaller metal−ligand species is the charged fragment. In other cases, ligand decomposition can occur, and the metal complex loses smaller stable neutral fragments. Yet another dissociation pathway is photoinduced charge transfer, as we have seen with several $M^+(\text{benzene})_n$ systems.[21] Fragmentation of these complexes yields a charged organic and a neutral metal atom by either direct excitation into a charge-transfer state at an energy above the dissociation limit or via an electronic curve crossing. For many metal ion−ligand systems, ligand elimination is expected on the basis of the structural stability of the ligand studied. However, because COT is less stable and can dissociate to form stable species such as benzene, ligand decomposition reactions may be expected in these systems, and this is in fact observed.

Experimental Section

The experimental apparatus has been described previously.[26] Clusters are produced via laser vaporization (355 nm) in a pulsed nozzle cluster source and mass analyzed in a reflectron time-of-flight mass spectrometer. By using a "cutaway" type rod holder, a free expansion of excess COT seeded in Ar produces clusters of the form $M^+(C_8H_8)_n$ efficiently. The molecular beam is skimmed from the source chamber into a differentially

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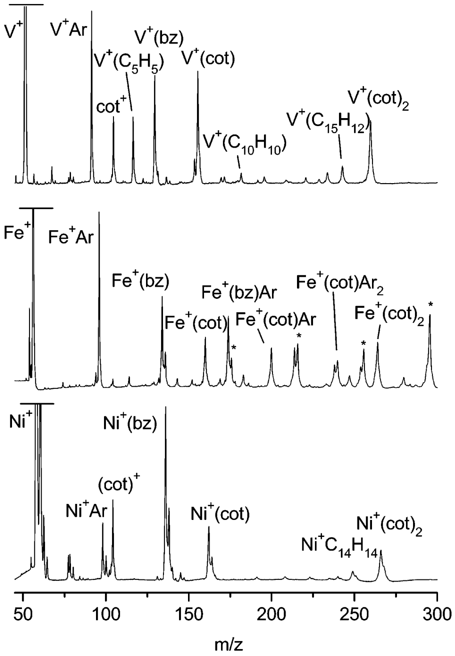

Figure 1. Time-of-flight mass spectra for V, Fe, and Ni−COT complexes formed in an Ar expansion. The solid line at the top of each mass spectra indicates that they have been cropped to highlight the complexes of interest. The $*$ denotes complexes of the form $M^+(Ar)_n$.

pumped mass spectrometer chamber. Cations are pulse accelerated into the first flight tube and mass selected by pulsed deflection plates located just prior to the reflection region. The ions of interest are then intersected by the second or third harmonic output of an Nd:YAG laser system, at 532 and 355 nm, respectively. Excitation of these ions leads to subsequent fragmentation. Parent and fragment ions are mass analyzed in the second flight tube and detected using an electron multiplier tube and a digital oscilloscope (LeCroy 9310A). Data are transferred to a PC via an IEEE-488 interface.

Results and Discussion

The mass spectra of clusters obtained for COT with vanadium, iron, and nickel are shown in Figure 1. These have been cropped to show the ions of interest, with a solid line denoting where the intensities of the atomic ions are off scale. As shown, the higher mass region is dominated by clusters of the form $M^+(C_8H_8)_n$, which correspond to intact COT adducts with atomic metal cations. Because metal atom recombination is limited in this particular cluster source configuration, multiple metal atom species, and in particular the possible multiple decker sandwich clusters, are not produced efficiently. Also present at lower mass are complexes associated with COT dissociation products from the plasma chemistry, that is, M^+(benzene), and the COT cation without any metal. The mass spectrum for vanadium also shows a significant amount of $V^+(C_5H_5)$. $Ag^+(COT)_n$ (not shown), on the other hand, forms only COT adducts with no ligand decomposition products. No clusters of pure metal, COT clusters, or multiple decker sandwiches are observed in any of these systems. However, complexes of M^+Ar are observed for all species and M^+(ligand)Ar are formed extensively for M = Fe. Smaller peaks can be attributed to metal−water complexes or metal oxides from trace impurities either in the gas line or on the surface of the ablation target.

To begin the study of these metal−ligand complexes, it is first interesting to know how the ligand itself behaves. Neutral COT has been known to undergo a retro-cyclotrimerization reaction to form benzene and acetylene when exposed to light.[27] It is therefore interesting to see if similar behavior occurs for the COT cation. Figure 2 shows the photofragmentation mass spectrum of COT^+. For this study, the $C_8H_8^+$ cation was mass selected and excited at 532 nm. These data, as with all fragmentation spectra in this study, are generated with a previously described computer difference method.[26] A mass spectrum recorded with the laser on is subtracted from one with the laser off, producing a negative-going parent ion peak (i.e., depletion) and positive fragment peaks. The UV/vis spectrum of the COT cation has been reported previously by Fu and Dunbar using photodissociation spectroscopy.[28] There is a strong resonance near 500 nm in this spectrum, and consistent with this we observe efficient fragmentation at 532 nm. Fragmentation occurs by the loss of neutral H, leaving $C_8H_7^+$, and by the loss of neutral C_2H_2, leaving the benzene cation. A small amount of $C_7H_4^+$ is also observed from the loss of neutral CH_4. Fragmentation patterns with similar masses and intensities are observed in the electron impact and photoionization mass spectra of COT^+.[29,30] In these previous experiments, appearance energies were recorded for $C_8H_7^+$ (10.90 ± 0.10 eV)[29] and for $C_6H_6^+$ (9.40 ± 0.05 eV).[30] When the IP of COT (8.2 ± 0.2 eV)[31] is subtracted from each of these measurements, the approximate energy for COT^+ dissociation into these channels can be calculated. This works out to 2.7 ± 0.2 eV for $C_8H_7^+$ and 1.2 ± 0.2 eV for $C_6H_6^+$. The incident photon energy in this experiment (532 nm = 2.32 eV) is very close to these dissociation values. Hence, the photochemistry here could conceivably come from two different one-photon processes occurring in parallel, although we cannot rule out resonance-enhanced two-photon processes.

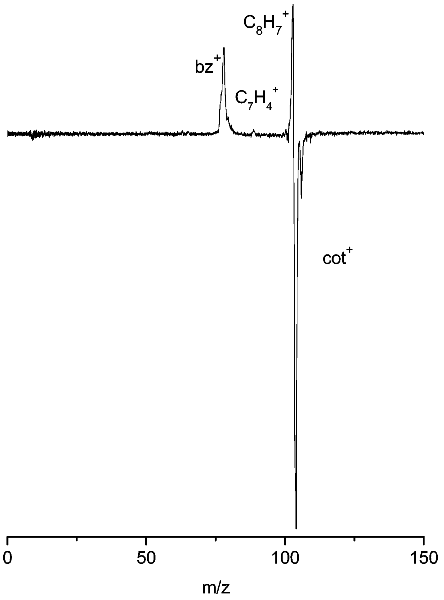

Figure 2. Photofragmentation mass spectrum of cyclooctatetraene (COT) cation at 532 nm. The spectrum is generated by subtracting the mass spectrum with the laser off from the mass spectrum with the laser on leaving a negative-going peak for depleted complexes and positive peaks for fragments.

As a first example of a metal−COT system, we examine Ag^+(COT). Ag^+ has a d^{10} closed-shell electronic configuration and the electronic structure of the complex should be relatively simple. The photofragmentation mass spectrum of Ag^+(COT) at 355 nm is shown in Figure 3. The doublet in the negative-going parent peak is attributed to the two naturally occurring isotopes (107, 109) of Ag resolved in the Ag^+(COT) parent.

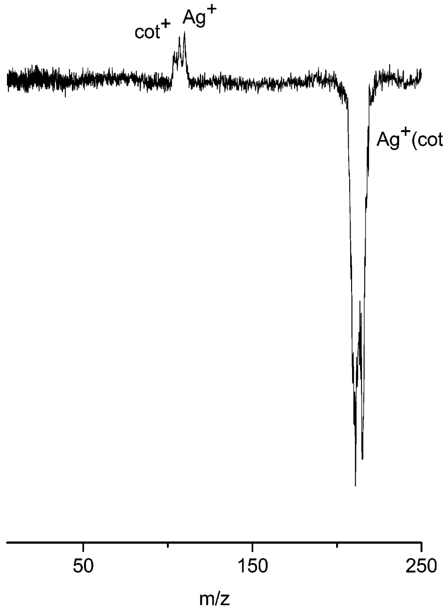

Figure 3. Photofragmentation mass spectrum of Ag^+(COT) at 355 nm. The complex fragments via two dissociation pathways: simple ligand elimination and photoinduced charge transfer.

What appears to be a triplet is observed in the positive-going fragment portion of the spectrum. Actually, this triplet can be attributed to two distinct fragmentation channels: the Ag^+ fragment (mass 107 and 109) and the COT^+ fragment ion at mass 104. The former occurs from simple ligand elimination and the latter is a result of photoinduced charge-transfer dissociation. Just as there was no evidence of COT decomposition due to plasma chemistry in the mass spectrum of Ag^+(COT), there also is no ligand decomposition upon photofragmentation. This experiment was performed with low-laser fluence to ensure single-photon processes. At higher photon energy, subsequent fragmentation of COT^+ leads to the appearance of benzene$^+$. Previous work in this lab and others has demonstrated similar behavior from Ag^+(ligand) systems.[21,31] In this previous work, it was shown that an upper limit could be placed on the metal ion−ligand bond energy according to the following equation:

$$D_0 \leq h\nu - \Delta \mathrm{IP}$$

where $h\nu$ is the incident photon energy and ΔIP is equal to the difference in the ionization potentials between the metal and the ligand. In Ag^+(COT), an upper limit of $D_0 \sim 2.8$ eV can be derived for excitation at 355 nm with ΔIP equal to $8.2 - 7.6 = 0.65$ eV. However, this value is approximate because the ionization potential of COT has an uncertainty of ±0.2 eV. Likewise, as we have discussed previously,[21] these energetics rely on the assumption of cold ions and the absence of any multiphoton absorption processes. Our experiments are designed to satisfy these conditions, but it is difficult to guarantee them. Therefore, it would be useful to have more accurate collisional dissociation experiments for these ions.

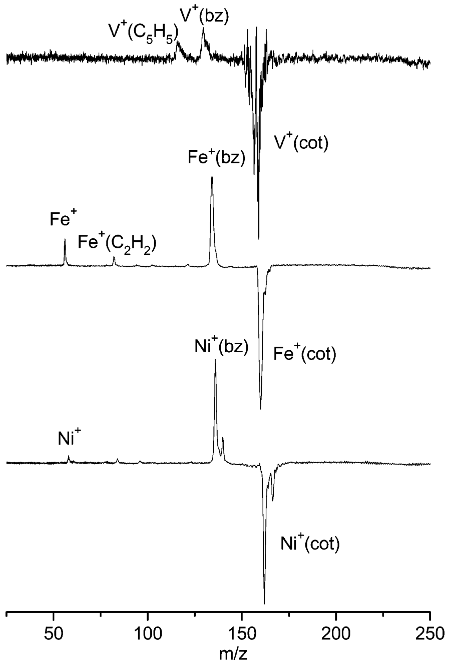

Figure 4. Photofragmentation mass spectra of V, Fe, and Ni cation mono-COT complexes at 355 nm.

The photofragmentation mass spectra for the M^+(COT) (M = V, Fe, Ni) systems with excitation at 355 nm are shown in Figure 4. Similar fragmentation patterns are seen with 532 nm, but with lower signal levels. The noise level is greater in the vanadium system, reflecting the lower photodissociation efficiency for this ion at this wavelength. All three systems are quite different from the Ag^+(COT) system. There is no evidence for any charge transfer in these systems. Instead, the major fragmentation channel is the loss of C_2H_2 (i.e., acetylene) and the production of $M^+(C_6H_6)$, that is, the metal−benzene complex. The different channels observed for these metals indicate perhaps a higher reactivity or a different bonding configuration for the transition-metal species with partially filled d shells. The closed-shell Ag^+ system would have more electrostatic bonding, while the open-shelled species could have some covalent character in their binding. If the bonding is stronger in the V, Fe, and Ni systems than it is in the Ag complex, the charge-transfer channel would lie at higher energy, perhaps explaining why it is not seen here. Although there is some evidence for elimination of intact COT in the nickel and iron complexes, it is not the main fragmentation pathway. It is also interesting that the channel corresponding to the loss of neutral H that was prevalent for the dissociation of COT^+ is absent from all metal ion−COT complexes. This probably indicates that the formation of a $M^+(C_8H_7)$ complex is energetically unfavorable compared to other possible channels. As noted earlier, the appearance energy of this channel in COT^+ is 1.5 eV higher in energy than in the $C_6H_6{}^+$ channel. It is possible that the photon energy (355 nm = 3.49 eV) is not high enough in these metal−ligand systems to access this fragmentation pathway.

In many organometallic systems, stability is associated with 18 π electrons.[19,20,25] These monoligand systems are well shy of this number and so the relative stability of fragment ions must be examined in other contexts. The main fragmentation channel for V^+, Fe^+, and Ni^+ is the loss of neutral C_2H_2 to form M^+(benzene) complexes. This type of retro-cyclotrimerization of COT to benzene is seen in the photodissociation of COT^+ as well as in temperature-programmed desorption (TPD) experiments on Pt[32] and TiO_2[33] surfaces. First-row transition-metal cation−benzene complexes are relatively strongly bound. The dissociation energies of the relevant complexes are listed in Table 1.[34] High binding energies of the first-row transition metals to benzene make the formation of such products quite favorable. The lower binding energy of Ag^+ to benzene might explain why metal−benzene formation is not seen upon photodissociation of its COT adduct. Another likely mechanism

TABLE 1: Metal−Ligand Bond Energies for Various Metal−Benzene Complexes

species	D_0 (eV)[a]
$V^+(C_6H_6)$	2.42
$Fe^+(C_6H_6)$	2.15
$Ni^+(C_6H_6)$	2.42
$Ag^+(C_6H_6)$	1.62

[a] Reference 34.

for the formation of these benzene complexes is excitation into metal cation-based excited states, which then lead to reaction with the COT ligand. The open-shelled transition-metal cations all have low-lying excited states, and there will be molecular states of the complexes correlating to these that can be excited. Excited states of transition-metal cations are often more reactive than ground states. Ag^+, however, has no low-lying atomic excited states, and therefore the only molecular state for the Ag^+(COT) complex is likely one correlating to the charge-transfer asymptote. This could explain the lack of dissociative fragmentation in this system.

While the formation of M^+(benzene) fragments could be expected, it is surprising that we also detect an $M^+(C_5H_5)$ fragment in the V^+ complex. $V^+(C_5H_5)$ appears here with an intensity almost equal to that of the V^+(benzene) fragment. The same kind of $M^+(C_5H_5)$ fragment is detected, but small, for Fe^+ and it is not detected for Ni^+. It is well known that C_5H_5 is not aromatic but can become so as the cyclopentadienyl anion when it receives charge donation from metal in a complex.[19] The stability of ferrocene occurs by this mechanism, as two electrons from the metal core are donated to the two cyclopentadienyl ligands, thus stabilizing them and giving the overall complex 18 electrons.[19] It is likely that a similar charge-transfer mechanism can occur to stabilize these monoligand complexes. Because the complexes studied here have a net charge, the metal could carry an effective oxidation state of +2 by donating one electron to stabilize C_5H_5, forming a complex of the nominal form $[M^{2+}(C_5H_5)^-]^+$. The tendency to do this should vary with the second ionization potential of the metal. The second IP of vanadium is in fact the lowest of the three metals studied here at 14.7 eV while those of Fe and Ni are 16.2 and 18.2 eV,[35] respectively. It is then reasonable that the vanadium cation is more likely to donate electron density to stabilize the C_5H_5 moiety. The higher second IP of Fe decreases the likelihood of this process, consistent with the low intensity of this photofragment, while the second IP of Ni is too high to allow the $Ni^+(C_5H_5)$ species to form. If this logic is correct, one might expect other metals with low second IPs, such as the lanthanides, to exhibit similar behavior. This has in fact been observed in our lab,[36] where M^+(COT) complexes of Sm^+, Dy^+, and Nd^+ (second IPs of 11.1, 11.7, and 10.7 eV, respectively)[35] also photodissociate to produce the corresponding $M^+(C_5H_5)$ fragments.

Complexes with two COT ligands were also studied to investigate the stability of sandwich structures. The photofragmentation mass spectra for $V^+(COT)_2$, $Fe^+(COT)_2$, and $Ni^+(COT)_2$ at 355 nm are shown in Figure 5. The fragmentation patterns at 532 nm are similar to these but with lower signal to noise. $Ag^+(COT)_2$ did not fragment at either wavelength and, therefore, is not shown. All three di-COT complexes fragment primarily by the elimination of an intact COT unit. This is different from the mono-COT systems in which further ligand decomposition is seen as the primary dissociation pathway. This could indicate that the second COT ligand is less strongly bound than the first. This is not surprising if charge transfer from the metal is important in the bonding of these metal−COT complexes. COT requires two electrons to achieve aromatic character, and these metals just do not have enough electron-donating character to satisfy this need for two COT ligands. All three complexes show further fragmentation to M^+(bz) as is seen with the mono-COT complexes. It is not possible for our experiment to determine if this is a sequential process or a parallel fragmentation pathway. These same fragments are still seen at lower laser fluence, but power dependence studies cannot distinguish between a single-photon process and a resonance-enhanced two-photon process that has much higher cross section for one step.

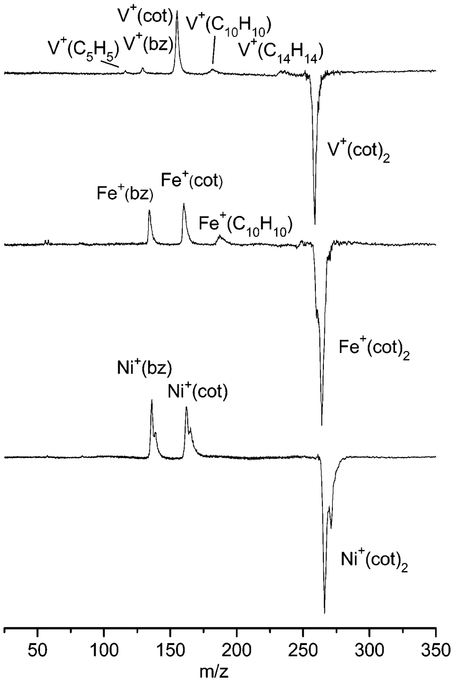

Figure 5. Photofragmentation mass spectra of V, Fe, and Ni cation di-COT complexes at 355 nm. These species fragment primarily by loss of intact COT molecules. Subsequent fragmentation follows the same patterns as observed for the mono-COT complexes.

$V^+(COT)_2$ has a minor fragmentation channel corresponding to the loss of C_2H_2, and both $V^+(COT)_2$ and $Fe^+(COT)_2$ have channels corresponding to the loss of C_6H_6, resulting in $M^+(C_{10}H_{10})$ fragment ions. This latter fragmentation is particularly interesting because $M^+(C_{10}H_{10})$ could correspond either to a M^+(COT)(acetylene) complex or to a $M^+(C_5H_5)_2$ complex analogous to ferrocene. Both Fe and V complexes with two cyclopentadienyl (Cp) ligands are well known in the condensed phase,[25] and the possibility of observing these complexes as dissociation products is intriguing. For either structure, the Fe and V complexes of $M^+(C_{10}H_{10})$ have a total of 17 and 16 electrons, respectively, and electron counts this close to 18 can result in relatively stable complexes.[25] $Ni^+(C_{10}H_{10})$, on the other hand, would have 19 electrons, which does not lead to stable complexes.[25] Photodissociation measurements also make it possible to investigate the structures of these $M^+(C_{10}H_{10})$ ions. Because they are observed as plasma chemistry products in the mass spectra of V and Fe (see Figure 1), it is possible to mass select them and observe their fragmentation patterns. The photofragmentation mass spectra of $V^+(C_{10}H_{10})$ and $Fe^+(C_{10}H_{10})$ at 532 nm are shown in Figure 6. The primary fragment for both species is the loss of neutral C_2H_2 to form M^+(COT), with some formation of M^+(bz). This fragmentation pattern as well as the lack of any $M^+(C_5H_5)$ fragments indicates that these species are most likely the $M^+(COT)(C_2H_2)$ ions and not the ferrocene-like structures. This structure is apparently preferred

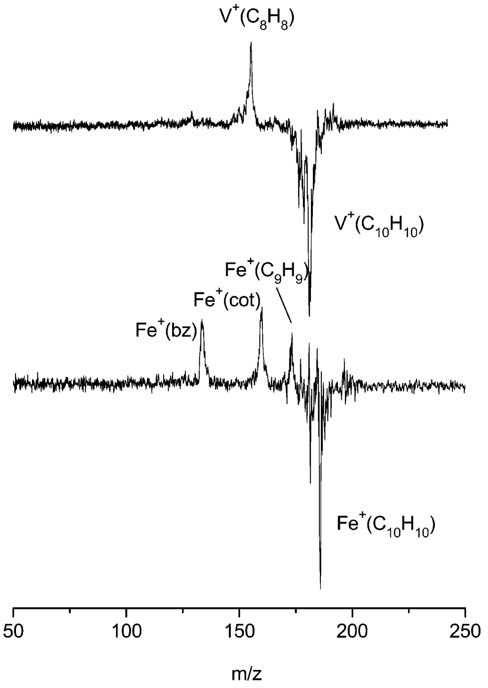

Figure 6. Photofragmentation mass spectra for $V^+(C_{10}H_{10})$ and $Fe^+(C_{10}H_{10})$ at 532 nm. Fragmentation patterns suggest that these complexes do not have ferrocene-like structures.

because it leads to a species with nearly 18 electrons, with benzene as an excellent neutral leaving group, without the large-scale rearrangement necessary for the formation of ferrocene-like complexes.

Another interesting ion formed as a minor channel in the fragmentation of $Fe^+(C_{10}H_{10})$ is $Fe^+(C_9H_9)$. This ion is somewhat puzzling as CH is not generally considered to be a good neutral leaving group. It is possible that this complex could be Fe^+(cyclobutadiene)(Cp). Although cyclobutadiene does not exist on its own, it can be stabilized by a metal center, particularly in complexes with Fe, Co, and Ni.[37,38] Unfortunately, this species is not directly generated in the plasma and therefore could not be studied further.

As a final example of metal−COT complexes, we decided to make and study mixed species of the form M^+(COT)(benzene). If dissociation in these species proceeds by COT decomposition, it would be possible to produce $M^+(bz)_2$ or M^+(bz)(Cp) complexes as fragments. Figure 7 shows the fragmentation of V^+(COT)(bz) and Fe^+(COT)(bz) complexes. As indicated, the primary process in these systems is the loss of benzene to form the M^+(COT) fragment ion. At higher laser power, the smaller fragments that were formed by the fragmentation of these M^+(COT) ions are also seen. In data not shown, the corresponding Ag^+ and Ni^+ complexes were also studied and they produced these same M^+(COT) fragment ions. The data shown is for fragmentation at 532 nm, but all four metal complexes were also studied at 355 nm with the same result. This fragmentation behavior is surprising, because it indicates that these metal ions bind more strongly to COT than they do to benzene. As we discussed in our earlier work on mixed complexes,[13] competitive elimination experiments can be used to determine relative ligand binding energies, as long as photoexcitation does not accidentally access some resonance leading to dissociation on an excited state potential. When excitation occurs by excited state absorption followed by internal conversion and dissociation in the ground state, the more weakly bound ligand will be preferentially eliminated first. Because all of these complexes exhibit the same behavior at both 532 and 355 nm, we can safely rule out excited state resonances and thus conclude that these metal cations bind more strongly to COT than they do to benzene. The benzene binding energies listed in Table 1 are therefore lower limits for the corresponding M^+(COT) binding energies. Stronger binding to COT than to benzene can be rationalized in at least two ways. Because COT is larger than benzene, its polarizability should be somewhat greater, thus enhancing the charge-induced dipole electrostatic component in bonding. However, the larger effect may be the greater amount of charge transfer in M^+(COT) binding. Because COT achieves greater stability by accepting charge from the metal ions and benzene is already aromatic without such charge donation, the charge-transfer interaction should be greater in the COT complexes. This could explain the apparent stronger bonding in these complexes. To our knowledge, there are no previous studies of M^+(COT) dissociation energies, nor have these binding energies been calculated. These studies would be useful for future investigations.

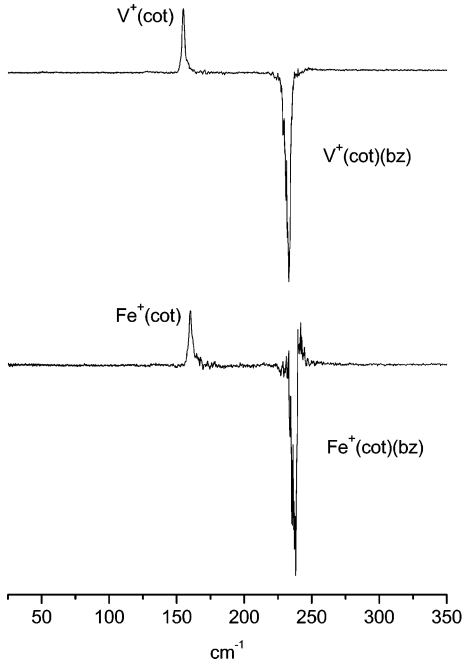

Figure 7. Photofragmentation mass spectrum for V^+(COT)(bz) and Fe^+(COT)(bz) at 532 nm.

The results and trends reported here suggest that the binding of transition metals to COT can be quite strong and that partial charge transfer from the transition metal is at least partly responsible for the stability of these complexes. It is therefore only natural to consider the structure of COT in these complexes and its possible distortion toward planarity that might occur when metal−ligand charge transfer occurs. Unfortunately, our experiment cannot distinguish in any way between η^8, η^6, or η^4 configurations that might be expected for the binding here. However, future theoretical studies may be able to explore these binding configurations for the different transition-metal complexes with COT to investigate the binding energetics suggested here.

Conclusions

Transition-metal ion−cyclooctatetraene complexes of V, Fe, Ni, and Ag were produced by laser vaporization and studied by photodissociation at 355 and 532 nm. The mass spectra show simple adducts of $M^+(COT)_{1,2}$ as well as other smaller complexes formed via COT decomposition in the laser plasma. Mass-selected photodissociation measurements on each complex showed various metal-dependent fragmentation channels. Ag^+(COT) was the only complex that demonstrated both simple ligand elimination and photoinduced charge transfer. The mono-COT complexes of V, Fe, and Ni all show extensive ligand decomposition upon photofragmentation, yielding $M^+(C_6H_6)$ as the main fragment ion. Photofragmentation of both V and Fe mono-COT complexes also produced $M^+(C_5H_5)$ and this is attributed to their relatively low second IPs, which allow donation of electron density to the C_5H_5 ligand that stabilizes it. Fragmentation patterns for di-COT complexes of V, Fe, and Ni were also recorded. These systems exhibit primarily the elimination of intact COT ligands, indicating that the second ligand is more weakly interacting with the metal than the first. V and Fe di-COT complexes also fragment to form $M^+(C_{10}H_{10})$. Further investigation of these complexes indicates that they have an $M^+(COT)(C_2H_2)$ structure rather than a ferrocene-like structure. Dissociation of mixed complexes containing both COT and benzene takes place by the loss of benzene. This suggests that the binding energies of these transition-metal cations with COT are greater than those with benzene.

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