The vibrational assignments based upon carbon-13, oxygen-18, and deuterium isotopic shifts are in general agreement with those of Alcock and Mile[9] that C–O stretches for the POZ fall in the 900–1000-cm^{-1} range and that the strong O–O–O stretching mode is substantially lower (697 cm^{-1} in the case of diisopropylethylene ozonide) based on comparisons with cyclic ethers and peroxides[9] and on very recent unpublished oxygen-18 substitution results.[11] These assignments are in disagreement with the tentative ones of Hull et al.[8] based on a simple comparison with ozone. Clearly, carbon-13 and oxygen-18 isotopic data are needed to make correct vibrational assignments.

Bonding in the Primary Ozonide. The most interesting part of the POZ molecule is the –O–O–O– group, and information on the binding in this group can be obtained through comparison to similar molecules containing the trioxygen linkage. Table V shows that the O–O stretching modes for the POZ are substantially lower than ozone, inorganic ozonide, and bis(trifluoromethyl)trioxide values. This comparison shows that the O–O–O bonds in the POZ are comparatively weak σ bonds, particularly relative to the "standard" O–O single bond fundamental at 880 cm^{-1} in hydrogen peroxide.[19] The instability of the POZ to decomposition by rupture of an O–O bond is also indicative of weak O–O bonds.

On the other hand, the C–O stretching modes of the POZ, 983 and 927 cm^{-1}, are just below the strong C–O stretching modes of the SOZ at 1079 and 952 cm^{-1} and the C–O stretching mode of CH_3OH at 1034 cm^{-1},[20] which shows that the C–O bonds in the POZ are only slightly weaker than normal single bonds.

Reactions Occurring in Solid Xenon. Finally, the reaction of ethylene and ozone proceeds at a finite rate in solid xenon at 80 K. Nelander and Nord have shown that the rate of formation of POZ in solid CO_2 is consistent with a 4 ± 1 kcal/mol activation energy, in agreement with the gas-phase value.[12] The POZ is believed to be formed by a concerted reaction; indirect support for the concerted mechanism may be derived from the failure to observe any additional absorptions in the xenon experiments that might be due to a $\cdot CH_2CH_2OOO\cdot$ intermediate. Rearrangement of POZ to SOZ occurs within the matrix cage as is shown by the lack of h_4 and d_4 SOZ species in the CH_2CD_2 experiments. Although formaldehyde was a major reaction product, no evidence was found for additional transient species such as dioxirane or methylene peroxide.

The relative yields of the several reaction products were not changed with reaction temperature in different experiments. Based on the SOZ and POZ band absorbances at 802 and 727 cm^{-1}, respectively, a comparable yield of each species was produced, and there was no measurable difference in the relative SOZ and POZ yields for reaction in the 80–100 K range. Since the warming–cooling cycles decreased sample transmission and photometric accuracy, a very small change (<10%) in the relative SOZ and POZ yields over this limited temperature range cannot be determined.

Conclusions

Ozone and ethylene react upon diffusion at approximately 80 K in solid xenon to form the POZ and SOZ products. The latter absorptions were identified by preparing the SOZ species in Freon solution for matrix spectroscopic study; the remaining POZ absorptions were more photosensitive than the SOZ bands. Isotopic substitution ($^{16,18}O_3$, $^{18}O_3$, CH_2CD_2, C_2D_4, and $^{13}C_2H_4$) provides a sound basis for characterizing the POZ vibrational modes. The C–O stretching vibrations at 983 and 927 cm^{-1} are reasonable values for single bonds; however, the symmetric and antisymmetric O–O–O stretching modes at 846 and 647 cm^{-1}, respectively, are unusually low values for single bonds, consistent with the instability of the POZ species to O–O bond rupture. A 1/2/1/1/2/1 relative intensity sextet for the strong 647-cm^{-1} band in the 50% oxygen-18 enriched experiment confirms the POZ structural arrangement.

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Secondary Ion Mass Spectra of Coordination Compounds and Organometallics

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Abstract: The extension of secondary ion mass spectrometry (SIMS) to the direct analysis from surfaces of preformed, well-defined, coordination compounds and organometallics is presented. In both instances, the SIMS spectra contain ions characteristic of molecular weight and structurally diagnostic fragment ions. Secondary ions are produced by several mechanisms, including cationization, electron transfer, and direct sputtering of precharged species. Ammonium chloride and sodium chloride were investigated as room-temperature matrices to decrease the abundances of ions resulting from intermolecular processes and increase the S/N ratio for peaks corresponding to structurally informative ions. Empirical structure–spectral correlations developed in this study aid in the definition of surface structure on a scale particularly appropriate to catalysis research.

The unique catalytic properties of many transition-metal complexes have provided some of the impetus for the synthesis of increasingly complex molecules. Mass spectrometry has been used extensively in the characterization of such compounds[1] and continued expansions and refinements of the technique have been chronicled in regular reviews.[2,3] Since many coordination complexes and organometallic compounds are prone to thermal decomposition, methods which avoid macroscopic vaporization of the sample, such as field desorption and plasma desorption mass spectrometry, have seen some application in this area. Use of a surface analysis technique such as secondary ion mass spectrometry (SIMS) can also obviate such a requirement. Recent applications of SIMS to the analysis of organic compounds[4] have revealed that stable gas-phase complexes, such as those between transition metals

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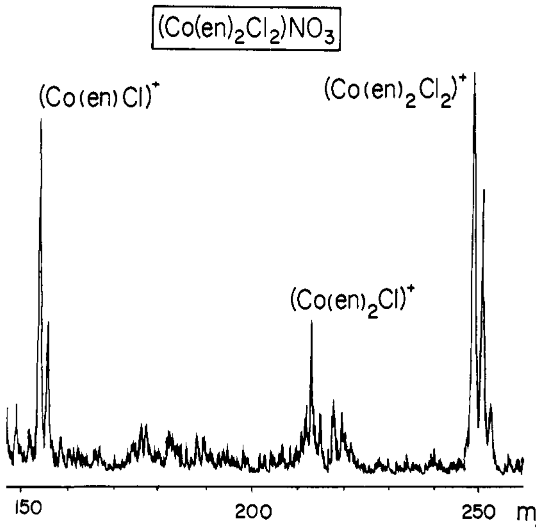

Figure 1. SIMS spectrum of *trans*-$[Co(en)_2Cl_2]NO_3$. The spectrum is independent of the nature of the counterion.

and ligands such as phenanthroline, can constitute the main secondary ions in the spectra of the ligands sputtered from a metal support.[5] The logical extension of SIMS to the direct analysis of preformed, well-defined, metal complexes of both coordination compounds and organometallics is reported in this paper and constitutes, to our knowledge, the first comprehensive SIMS study of this type.

Two types of compounds have been investigated: those which are electrically neutral and those in which the metal is present in a cationic species. A fair degree of success was expected based on previous results showing metal cationization of neutral organic molecules[6-8] and successful analysis of organic salts.[9,10] In both instances, the SIMS spectra obtained did indeed contain ions characteristic of molecular weight as well as structurally diagnostic fragment ions.

Several general processes have been shown to form secondary ions when a beam of high-energy ions impacts a molecular solid surface. The first is cationization, in which the cation C^+ attaches to an intact molecule of the sample, forming the adduct ion $(C + M)^+$. Protonation can be considered the simplest example of the cationization process. The second process involves electron transfer and leads to the formation of $M^{+\cdot}$ and $M^{-\cdot}$ radicals. Finally, in the case of a sample which (i) is already present in the form of a salt or (ii) contains weak bonds which suffer heterolysis, direct sputtering of cations and anions into the gas phase occurs. We have found examples of all of these processes in this study of organometallic and coordination compounds, although the process of direct sputtering of preformed ions predominates since many of the samples were studied as salts.

Experimental Section

Positive ion SIMS spectra were obtained with a commercial Riber instrument utilizing an energy selector, a quadrupole mass filter, a Channeltron electron multiplier, and pulse counting electronics. A 5-keV argon ion beam was used to bombard the sample. Ion currents were held at or below 2×10^{-9} A/cm^2 to minimize beam damage. Operating pressure in the main chamber of the instrument was typically 1×10^{-8} torr or less. Spectra were obtained with the quadrupole scanning at the rate of 3 s/amu. The region below *m/z* 100 is not reported because of substantial contributions from surface contaminants. Spectra were reproducible from run-to-run on the same sample to ca. 10% relative abundance. Larger variations sometimes occurred when samples were independently prepared.

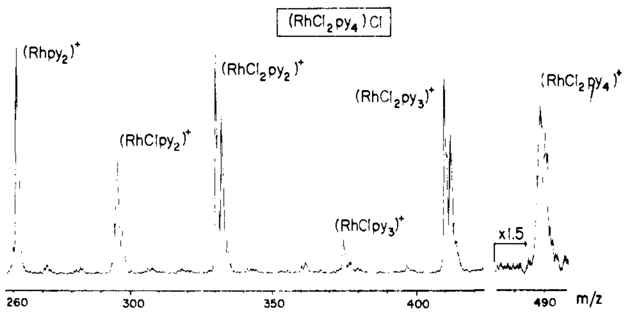

Figure 2. Partial SIMS spectrum of $[RhCl_2py_4]Cl{\cdot}5H_2O$ showing sequential ligand loss. Rhpy and Rh^+ ions are also observed.

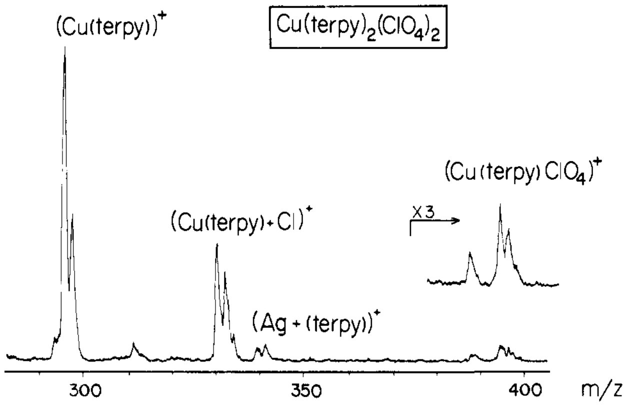

Figure 3. SIMS spectrum of $[Cu(terpy)_2](ClO_4)_2$. In addition to the copper-containing species, some silver cationization of the organic ligand is observed.

Samples admixed with an excess of ammonium chloride or sodium chloride were burnished onto silver foils of 1 cm^2 area which were abrasively cleaned. In general, use of a matrix in SIMS analyses increases the intensity of the sputtered secondary ions; this observation is discussed more fully in the following section. No charging effects for these samples were noted. A few of the metal complexes were obtained from commercial sources but most were available from earlier studies in our laboratory and were used without further purification.

Results and Discussion

(a) Positive Ion SIMS Spectra. Nitrogen-Containing Ligands. Cobalt(III) ethylenediamine compounds of the general formula *trans*-$[Co(en)_2Cl_2]X$, where en = ethylenediamine and X = Cl, Br, or NO_3, were analyzed by SIMS. The positive ion SIMS spectrum of the nitrate salt is shown in part in Figure 1. The base peak of the spectrum corresponds to the intact cation $[Co(en)_2Cl_2]^+$ at *m/z* 249. Fragment ions which correspond to the loss of Cl and the loss of (Cl + en) from the cation appear with relative abundances of 25% and 65%, respectively. All the ions show the appropriate isotope clusters. Identical spectra were obtained for the salts with Br^- or Cl^- as the counterion.

A portion of the SIMS spectrum of the pyridine (py) complex $[RhCl_2py_4]Cl{\cdot}5H_2O$ is shown in Figure 2. The intact cation is observed at *m/z* 489, 491, 493, and 495. A major fragmentation pathway for this ion involves sequential loss of the pyridine ligands to yield the ^{35}Cl ions at *m/z* 410 and 331. Ions formed by ejection of various combinations of pyridine and chlorine are also observed, but with lower abundances. Ions corresponding to $Rhpy_2^+$ and $Rhpy^+$ are comparable in abundance to the molecular cation. Loss of 27 amu (presumably HCN) from $Rhpy^+$ forms an ion at *m/z* 155. The monovalent Rh^+ ion at *m/z* 103 is also observed, but with a low abundance relative to all of the other fragment ions. Initial loss of chlorine from the intact cation is not observed.

The SIMS spectrum of $[Cupy_2](NO_3)_2$ contains a base peak corresponding to the $Cupy_2^+$ ion. The $Cupy^+$ ion is observed with a relative abundance of 50%. Fragmentation of the $Cupy^+$ ion by loss of HCN is not observed. No $Cupy_2^{2+}$ is noted and reduction to the monovalent cation in these cases predominates. In

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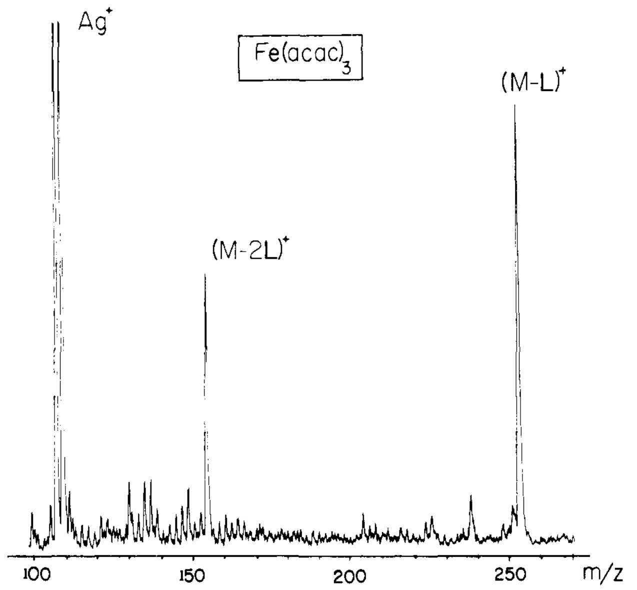

Figure 4. SIMS spectrum of Fe(acac)$_3$.

some experiments, however, a small amount of $CuPy_2NO_3^+$ is observed.

Compounds of the type Cu(terpy)X_2 where terpy is the planar tridentate 2,2′,2″-terpyridyl ligand and X is Cl or Br have also been investigated. The SIMS spectra of these compounds contain a base peak singly charged cation Cu(terpy)$^+$. An ion Cu(terpy)Cl^+ was observed in the spectrum of the chloride salt, but the analogous ion was not formed from the bromide salt. No other fragmentations were noted. The spectrum of the bis(terpyridyl) complex [Cu(terpy)$_2$] $(ClO_4)_2$ is shown in Figure 3. The most intense peak in this spectrum is once again the Cu(terpy)$^+$ ion; the monocation Cu(terpy)$_2^+$ is not observed. Ions corresponding to Cu(terpy)Cl^+ and Cu(terpy)ClO_4^+ are also observed.

The SIMS spectrum of Pd(bpy)$(NCS)_2$, where bpy is the 2,2′-bipyridyl ligand, contains a base peak at Pd(bpy)$^+$ and a fragment ion Pd(bpy)(NCS)$^+$ (25% relative abundance). A small amount of the ion Pd(bpy)Cl^+ is observed, presumably related to the presence of chloride from the admixed ammonium chloride salt. These ions are analogous to those observed in the Cu(terpy)X_2 spectra.

SIMS analysis of preformed phenanthroline (phen) complexes is of particular interest since ions such as (Cu + phen)$^+$ and (Cu + 2phen)$^+$ are present in the SIMS spectrum of phenanthroline sputtered from a copper support.[5,8] The spectrum of (dmp)$_2CuCl_2$ (where dmp is the 1,10-dimethylphenanthroline ligand) supported on silver contains peaks which correspond to the ions dmp$^+$ (30%), Cu(dmp)$^+$ (100%), and Ag(dmp)$^+$ (15%). The unsubstituted phenanthroline complex gives an analogous spectrum.

Oxygen-Containing Ligands. Acetylacetonate (acac) compounds have been exhaustively studied by a number of mass spectroscopic methods and the SIMS spectra of a few of these compounds are presented here for the sake of comparison. The spectra of Fe(acac)$_3$ and VO(acac)$_2$ recorded on the compound mixed with NH_4Cl (conditions which do not facilitate cationization) are shown in Figures 4 and 5, respectively. As shown later, quite different spectra can be recorded under conditions which promote cationization. In the SIMS spectrum of the iron compound, the base peak corresponds to loss of a single ligand, forming Fe(acac)$_2^+$. Loss of two ligands also occurs; the ion Fe(acac)$^+$ is observed with a relative abundance of 30%. Loss of $CH_3\cdot$ from Fe(acac)$_2^+$ occurs to give an ion at *m/z* 239 with a relative abundance of 10%. A small amount of silver-cationized acetylacetonate is observed. No intact molecular ion for the Fe(acac)$_3$ compound is observed. Similarly, the SIMS spectrum of Mn(acac)$_3$ contains a base peak ion Mn(acac)$_2^+$ and the ion corresponding to loss of two ligands, Mn(acac)$^+$. Again, no intact molecular ion can be observed (but see below). Several fragments of low abundance ($\leq$10%) are consistently observed in the spectrum: these include ions at *m/z* 238, 226, 225, and 207. The ions can be rationalized in terms of fragmentations of the acac ligand. The metal cation Mn^+ was present in the spectrum with an abundance about equal to that of Mn(acac)$^+$.

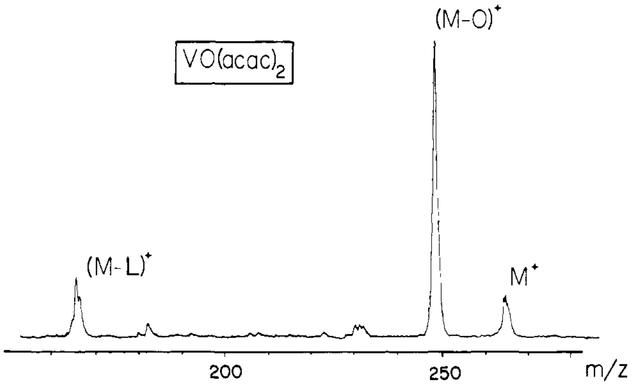

Figure 5. SIMS spectrum of VO(acac)$_2$. The intact molecular ion is observed. Loss of 16 amu parallels laser desorption results for similar compounds.

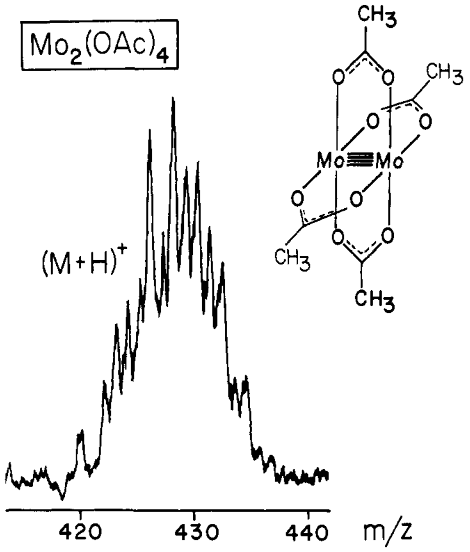

Figure 6. Molecular ion region of the SIMS spectrum of $Mo_2(OAc)_4$. The isotopic cluster indicates the presence of two molybdenum atoms.

The SIMS spectrum of VO(acac)$_2$ (Figure 5) contains a peak for the molecular ion at *m/z* 265. The base peak in this spectrum is formed by loss of oxygen from the molecular ion, presumably to form V(acac)$_2^+$. Loss of a single acac ligand to form the ion VO(acac)$^+$ also occurs. The ions V^+ (70%) and VO^+(20%) were also observed.

The molecular ion region of the positive ion SIMS spectrum of tetra-μ-acetato-dimolybdenum, $Mo_2(OAc)_4$, is shown in Figure 6. The (M + H)$^+$ ion cluster shown consititues the base peak in the spectrum, and the observed isotopic cluster is consistent with the presence of two molybdenum atoms. The only fragment ion observed is a small amount (10–15% relative abundance) of $Mo_2(OAc)_3^+$.

Other Compounds. The positive ion SIMS spectrum of the sulfur-containing compound [$RhCl_2$(dth)$_2$]PF_6 (where dth is the 2,5-dithiahexane ligand) contains the intact cation at *m/z* 417; no fragmentations are observed. Formation of this cation is independent of the nature of the counterion (both Cl^- and PF_6^- salts were examined).

The SIMS spectrum of silver diethyldithiocarbamate contains a base peak at *m/z* 116, which corresponds to the ion $SCNEt_2^+$. No peak corresponding to the intact species was observed.

The spectrum of Fe(dedtc)$_3$ (where dedtc is the diethyldithiocarbamate ligand), when obtained from an ammonium chloride matrix, contained a base peak at *m/z* 116 (presumably $SCNEt_2^+$) and a peak of only weak intensity corresponding to the Fe(dedtc)$^+$ ion. When analyzed directly from a silver surface or from a

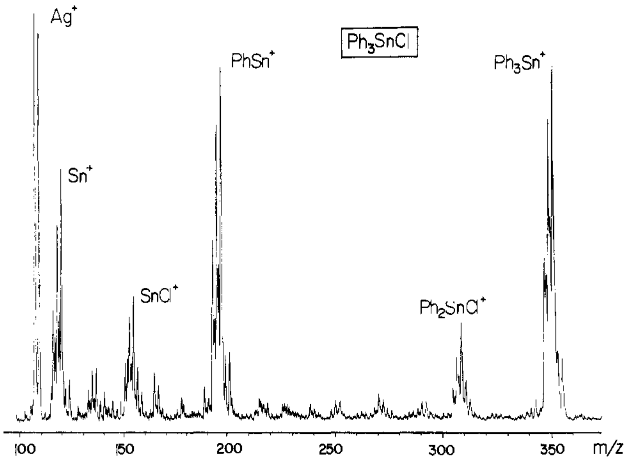

Figure 7. SIMS spectrum of triphenyltin chloride. Loss of a chlorine atom is preferred about 5:1 over loss of the organic radical.

sodium chloride matrix, however, a different spectrum was obtained. Although *m/z* 116 is still the base peak, the intensities of metal-containing ions and characteristic fragment ions were enhanced ($Fe(dedtc)_2^+$, 15%; $Fe(dedtc)^+$, 9%; $(Fe(dedtc)_2 - 32)^+$, 8%; $(Fe(dedtc)_2 - 60)^+$, 3%; $(CNEt_2)^+$, 40%). A small amount ($\sim$1%) of the intact molecular ion was observed. Cationization also occurred and provided more abundant species $(Na + M)^+$ (3%) and $(Fe + M)^+$ (5%), indicative of the molecular weight.

The SIMS spectrum of $(Cp)_2TiCl_2$ where Cp is the η^5-cyclopentadienyl ligand does not contain a peak for the molecular ion. The base peak in this spectrum corresponds to the ion $(M - 2Cl)^+$; other peaks include the heterolysis product: $(M - Cl)^+$, 63%; $(M - CpCl)^+$, 20%; $(M - CpHCl)^+$, 20%; and $TiCp^+$, 12%. Notably, no peak corresponding to the loss of a single cyclopentadienyl ligand is observed.

The SIMS spectrum of $[CpFe(CO)_2]_2$ was obtained with the use of a sodium chloride matrix (spectra obtained from an ammonium chloride matrix were irreproducible). The base peak in this spectrum was the $CpFe^+$ ion at *m/z* 121, and a large number of metal-containing ions were observed representing both cationization and fragmentation processes: $(Na + M)^+$, 5%; M^+, 5%; $(M - CO)^+$, 10%; $(M - 2CO)^+$, 15%; $(Ag + CpFe_2)^+$, 20%; $(M - 3CO)^+$, 15%; $(Cp_2Fe_2)^+$, 15%; $(Cp_2Fe)^+$, 50%; and $(CpFe_2)^+$, 25%. Atomic iron, Fe^+, was of about the same intensity as $CpFe^+$.

The spectrum obtained for the main group organometallic Ph_3SnCl (where Ph is phenyl) is given in Figure 7. The intact species is not observed. The cation Ph_3Sn^+ is the base peak in the spectrum. An ion almost as abundant is $PhSn^+$ at *m/z* 197. Ions of lower abundance include Ph_2SnCl^+, $SnCl^+$, and Sn^+. The spectrum of tetraphenylarsonium chloride contains a base peak Ph_4As^+ cation and two significant fragment ions, $PhAs^+$ and Ph_2AsCl^+.

(b) Comparisons with Mass Spectra Obtained by Other Methods. Field desorption (FD) mass spectra of compounds of the type $[Co(en)_2Cl_2]X$ have been reported.[11] For the chloride salts, the trans compounds did not yield an observable intact cation. Instead, the base peak corresponds to the loss of one of the en ligands from the cation. Loss of a single halogen atom was noted for some halogen and counterion combinations. On the other hand, the cis compound produced a base peak cation in the FD spectrum, and no fragmentations at all were observed. The SIMS spectrum of the trans compound is intermediate between these results in that it contains both the intact cation and fragmentations that are structurally informative.

The electron impact mass spectra of acetylacetonate compounds show considerable variation from study to study, although the spectra were obtained under nominally identical conditions.[12-14]

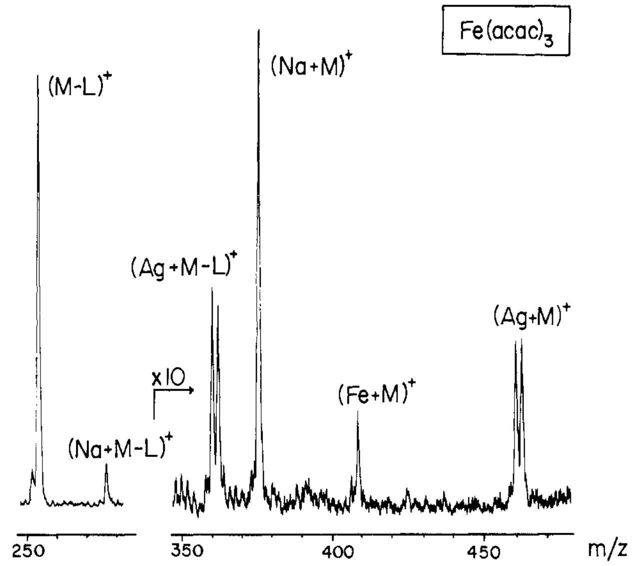

Figure 8. SIMS spectra of $Fe(acac)_3$, containing metal-cationized species. The $(Fe + M)^+$ ion is apparently formed in a self-cationization process.

It has been shown that some of these differences can be ascribed to thermal decomposition of these compounds in the vaporization system of the mass spectrometer.[15] In general, the electron impact spectra of both $Fe(acac)_3$ and $Mn(acac)_3$ contain molecular ions (albeit of low abundance), while their respective SIMS spectra do not. Otherwise the spectra contain ions representing the same fragmentations, although the abundances are different. Although both of these compounds are sensitive to thermal decomposition, that this is not the reason for the absence of molecular ions is shown by the observation in SIMS of intact molecules as cationized species. For example, when $Fe(acac)_3$ is analyzed from an ammonium chloride and sodium chloride matrix and care is taken to expose the silver metal support surface to the ion beam simultaneously, a variety of metal cationized species can be generated, as shown in Figure 8. Three abundant cationized species are observed: $(Na + M)^+$, $(Fe + M)^+$, and $(Ag + M)^+$, where M represents the intact molecule $Fe(acac)_3$. Loss of a single ligand from these cationized species produces the ions $(Na + M - acac)^+$ and $(Ag + M - acac)^+$. $Mn(acac)_3$ forms a self-cationized species $(Mn + M)^+$ but cationization of this compound by sodium or silver does not occur as readily as do the corresponding processes with the iron compound.

The SIMS spectrum of the $VO(acac)_2$ compound is unique in that the molecular ion is observed, and the base peak corresponds to loss of 16 amu, apparently oxygen, from the molecular ion. This contrasts with the electron impact mass spectrum of this compound in which this loss is not observed—rather, loss of 15 amu from the ligand forms the $(M - 15)^+$ ion. However, in the spectrum of the related vanadyl complex of 1-phenyl-1,3-butanedionate obtained by using a laser microprobe mass analyzer (LAMMA), this same loss of oxygen is observed, and loss of methyl from the ligand, although possible, is not observed.[16] This result suggests a similarity between the ionization methods of LAMMA and SIMS, and draws a clear distinction between these methods and the electron impact method. It has not been demonstrated that the oxygen loss observed in the SIMS spectrum involves the unique oxygen atom bonded to the vanadium. Such a loss would be noteworthy in that the vanadium oxygen bond is thought to be fairly strong.

In view of the large volume of work on the mass spectrometry of acetylacetonate complexes, it is expected that they can well define the processes by which secondary ions are sputtered from a surface. The energetics of the ionization and fragmentation processes have been reviewed.[17] Both positive and negative ion

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chemical ionization studies are available.[18-20] Modification of the ligand for better volatility or sensitivity has also been investigated[19,21,22] and exchange reactions in the ion source have been documented.[23,24] Much of this work was involved with the quantitative analysis of trace metals as chelates by mass spectrometry.[25,26] Fortunately, a byproduct of this interest was the delineation of the gas phase ion chemistry of these compounds which can now be used to advantage in fundamental SIMS studies.

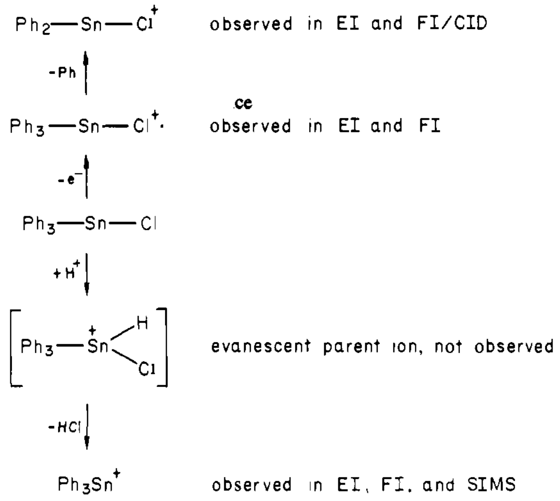
The electron impact mass spectrum of $Mo_2(OAc)_4$ has been reported and contains as its base peak the parent molecular ion.[27] In general, for various Mo_2^{4+} metal complexes, the electron impact mass spectra contain abundant molecular ions. The particular advantage of SIMS analysis of these compounds lies in the ability of the method to analyze these compounds directly from a surface where they may be catalytically active.[28]

Standard electron impact mass spectra of a number of bis(*N*,*N*-diethyldithiocarbamato) complexes have been reported.[29-31] The SIMS spectra presented here contain somewhat more fragmentation, and, in addition, the spectra are dependent on the matrix from which the coordination complex is sputtered. The silver surface itself may have a deleterious effect. Some interesting gas phase ion chemistry is evident in that ligand decomposition by loss of sulfur and sulfur plus ethylene occurs in the ionized ligand itself and in the $Fe(dedtc)_2^+$ ion, but apparently not in the $Fe(dedtc)^+$ ion. Too few compounds of this type have been analyzed by SIMS to discern the effects of metal–ligand charge-transfer processes described in the electron impact spectra.

The electron impact mass spectrum of Cp_2TiCl_2 at various electron energies has been thoroughly investigated.[32-34] At 50 eV, the base peak in the spectrum corresponds to loss of Cp and Cl from the molecular ion, while at 70 eV, loss of a single Cp ligand forms the base peak in the spectrum. The molecular ion of this compound is consistently observed in electron impact studies but the reported intensity of this peak varies. The SIMS spectrum is notably different. No molecular ion is observed, and loss of a single cyclopentadienyl ligand is not observed, although this is always a major fragment ion in the electron impact mass spectra. The SIMS results are quite surprising considering the strength of the titanium–chlorine bond in the free molecule.

The electron impact mass spectrum of $[CpFe(CO)_2]_2$ has been obtained by several workers.[35-38] The base peak in these spectra is the Cp_2Fe^+ ion, while in the SIMS spectrum it is the $CpFe^+$ ion. Although many of the fragment ions are common to the spectra obtained by both methods, a series of carbon monoxide losses following an initial loss of cyclopentadienyl ligand is observed in the EI spectra, but not in the SIMS spectrum. Cationized species are, of course, unique to the SIMS spectrum and provide decisive molecular weight characterization. The gas phase ion chemistry of the cyclopentadienyl metal carbonyl dimers has been carefully examined by electron impact methods. Several additional compounds will have to be analyzed by SIMS to establish the fragmentation schemes in the same detail.

Scheme I. Ion Chemistry of Triphenyltin Chloride as Studied by Secondary Ion Mass Spectrometry (SIMS), Electron Ionization (EI), Field Ionization (FI), FI with Collision-Induced Dissociation of a Mass Selected Ion (CID), and Chemical Ionization (CI)



The spectrum of Ph_3SnCl has been obtained by using electron impact mass spectrometry.[39] The base peak is reported to arise through loss of a phenyl group from the molecular species. The parent ion is observed, although with very low abundance. In contrast, the base peak observed in the SIMS spectrum corresponds to the loss of a chlorine atom to form Ph_3Sn^+. The EI results imply that the strength of the Sn–Cl bond is greater than that of the Sn–Ph bond in the isolated molecular ion, and this is confirmed by a recent field ionization (FI) study in which the collision-induced dissociations of the mass-selected molecular ion were studied.[40] Loss of chlorine in the SIMS spectrum and in the FI mass spectrum can be explained by invocation of an $(M + H)^+$ ion, not observed, which readily fragments by loss of HCl. In agreement with this postulate, a protonated molecular ion of this compound is not observed under standard chemical ionization (CI) conditions. Rather, the only peak observed in the isobutane CI spectrum corresponds to the Ph_3Sn^+ ion. The sum of experimental observations for triphenyltin chloride appears in Scheme I. Similar proposals of evanescent intermediates may account for unique SIMS behavior of other compounds (vide supra).

(c) Special Considerations of SIMS Analysis. The simplicity of sample preparation and ease of ionization inherent in the method facilitates analysis of these compounds by SIMS. For salts, the cation is nearly always an abundant ion in the spectrum and a clear identification is possible. By switching to negative ions, the nature of the counterion can be established. For example, SIMS analysis of $[RhCl_2(py)_4]PF_6$ yields PF_6^- as the most intense negative ion observed. On the other hand, neutral compounds may not form abundant molecular or quasimolecular ions.

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However, with the purposeful addition of sodium and/or transition metal salts, cationization of the intact molecule can be accomplished as was demonstrated for Fe(acac)$_3$. Cationization normally provides a relatively stable ion, although metal-cationized species are more stable than their protonated analogues (vide supra and ref 4 and 45). Although silver, sodium, and copper readily cationize most organic species, this same general reactivity does not seem to extend to preformed metal-containing complexes. Despite large excesses of sodium or silver ion, for example, several compounds did not form cationized species. Empirical correlations between observation of these cationized species and the sample matrix, the initial metal present, and the effect of the ligand are just now being worked out.

The use of the ammonium chloride matrix in these studies deserves comment. Analysis of a few of the compounds without this matrix has proven successful. However, it has previously been shown that the use of an ammonium chloride matrix vastly decreases the abundance of ions resulting from intermolecular processes which occur on the surface.[41] Thus to mitigate against such reactions, ammonium chloride was routinely used in this investigation. The salt also had a favorable effect on S/N ratios for peaks which are due to structurally characteristic secondary ions. Sodium chloride also shows some promise as a matrix with the added advantage that the sodium can act as a cationizing agent as well. The idea of using a matrix from which to ionize molecules in SIMS was first put forward by Michl, who used a frozen argon matrix for the analysis of hydrocarbons.[42] The salts employed here enjoy the singular advantage of forming a matrix at room temperature.

In some cases, as with Fe(dedtc)$_3$ or [CpFe(CO)$_2$]$_2$, ammonium chloride seems to prevent successful SIMS analysis, perhaps by forming a reactive protonated molecule. In these cases, sodium chloride provides a suitable inert matrix, and may in general be preferable when the Brönsted acidity of ammonium chloride is deleterious. The manipulation of the matrix to create various spectral effects is only now being developed. With appropriate choice, however, it should be possible to produce the cationic or cationized species for almost any organometallic compound. The ability of SIMS to produce different cationized species simultaneously allows for multiple checks on the molecular weight. The ability to cationize with a transition metal having a characteristic and highly visible isotope pattern is an advantage which should not be overlooked. This paper presents the first results of SIMS analyses of a range of different inorganic compounds and refinements will accrue from further investigations.

The mechanism of SIMS has not been considered in this paper although a resemblance to LDMS and other desorption ionization methods is implicit. Recently, explicit evidence for this connection has been found in the identity of the spectra of sucrose [(Ag + M)$^+$ and fragments], as recorded by both SIMS[43] and by laser desorption (LDMS),[44] and of vitamin B$_{12}$, as recorded by SIMS and by californium fission fragment mass spectrometry.[45] A full discussion of ionization processes in SIMS can be found elsewhere.[46]

(d) Conclusions and Directions. SIMS analysis of coordination compounds and organometallics produces secondary ions by the processes of cationization, electron transfer, and direct sputtering. The direct sputtering process invariably results in an abundant intact cation from compounds initially present as salts. Cationization produces ions which can contain several different metal atoms. The structure of these bimetallic species is not yet established, but further work should make a comparison with condensed phase bimetallic structures possible, facilitating analysis of surfaces with known or suspected catalytic activity by SIMS. Empirical rules of structure–spectrum correlation will help to define the surface on a scale appropriate to catalysis research. The effects of various catalyst activation strategies can be followed, as can the changes in surface molecular structure induced by catalytic activity. All interpretation of such SIMS spectra, however, must rely on the previous characterizations of well-defined surfaces and compounds such as this study has addressed.

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