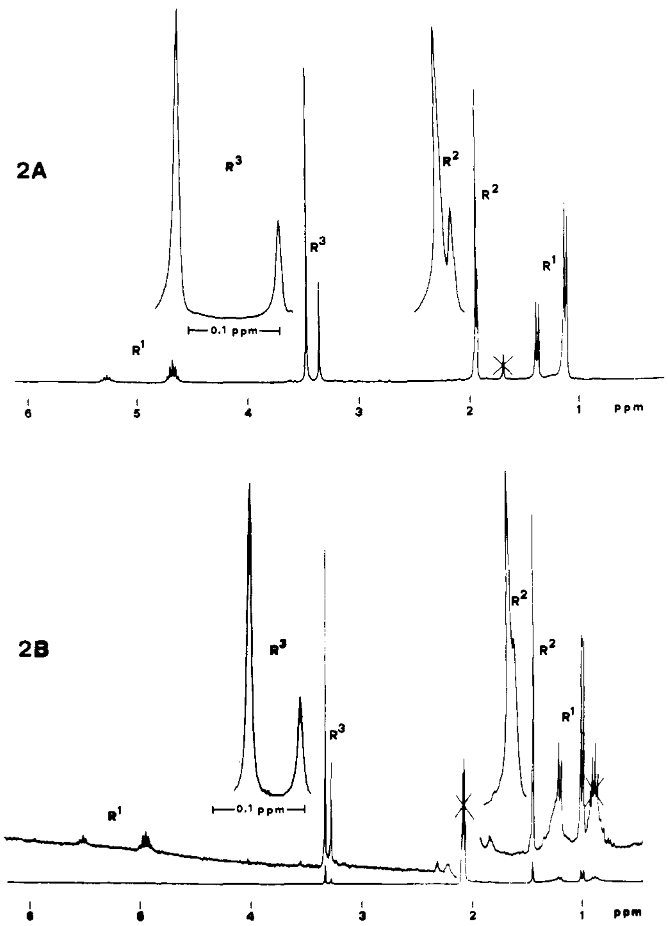

Figure 2. ^{1}H NMR spectra of *trans*-$PdCl_2(Pr^iMeC{=\!=}NNMePh)_2$ at 270 MHz and −10 °C: solvent $CDCl_3$ (A) and C_7D_8 (1000 scans) (B).

the trans ligand.[11]

In conclusion only two sets of NMR signals are present in these complexes in the range of temperature explored. They belong to two rotational isomers, A and B, and not to an intereacting and to a noninteracting hydrazone within the same molecule. Their coalescence necessarily requires a 180° rotation of the ligands about the Pd–N bond. Finally, any discussion on the variation of the chemical shifts of R^1 with temperature cannot be based solely on changes in the paramagnetic contribution of the metal, but changes in the relative influence of the trans ligand must also be considered.

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(5) Authors of ref 1 and 2 say that compounds I and II_2 are expected to have the same structure but leave an open question if they have pseudoanti (A) or pseudosyn (B) conformation.
(6) R^1 = Me and Pr^i refer to compounds I and II of the present text, respectively. R^1 = Et refers to *trans*-$PdCl_2(Et_2C{=\!=}NNMePh)_2$ earlier reported by us; see ref 3 and 4.
(7) Resonances (δ (ppm) from Me_4Si) of R^1, R^2, and R^3 are at 2.72, 2.10, and 3.57 in one set and at 3.04, 2.16, and 3.18 in the other. The first set is assigned to isomer A while the second set is assigned to B; the intensity ratio [A]/[B] is 0.6.
(8) High performance liquid chromatography was carried out under the following conditions: column, LiChrosorb DIOL 10μ, 50 × 0.42 cm i.d.; mobile phase, *n*-hexane–dichloromethane, 85:15 (v/v); flow rate, 2.0 cm^3/min at room temperature; detector R.I. The same technique was used to separate pure *trans*-$PdCl_2(Me_2C{=\!=}NNMePh)(Me_2C{=\!=}NNMe_2)$ from *trans*-$PdCl_2(Me_2C{=\!=}NNMePh)_2$ and *trans*-$PdCl_2(Me_2C{=\!=}NNMe_2)$; see below. F. Gasparrini, D. Misiti, G. Natile, and B. Galli, *J. Chromatogr.*, **161**, 356 (1978).
(9) The half band width was <1.5 Hz corresponding to 0.005 ppm.
(10) The resonances in $CDCl_3$ solution (δ (ppm) from Me_4Si; the first value refers to isomer A, the second value to isomer B) of *trans*-$PdCl_2(Pr^iMeC{=\!=}NNMePh)_2$ follow: R^1 (α-H), 4.96 and 5.29; R^1 (β-H), 1.13 and 1.39; R^2, 1.95 and 1.94; R^3, 3.48 and 3.37. The resonances (order same as above) of the same compound in C_7D_8 follow: R^1 (α-H), 4.93 and 5.50; R^1 (β-H), 0.99 and 1.19; R^2, 1.44 and 1.44_5; R^3, 3.32 and 3.27. The splitting of the R^2 protons was not observed by Postel et al.
(11) The resonances (δ (ppm) from Me_4Si; the first value refers to isomer A, the second value to isomer B) of $Me_2C{=\!=}NNMePh$ hydrazone (in compound I) follow: R^1, 2.67 and 3.11; R^3, 3.49 and 3.18. In the mixed complex, they are as follows: R^1, 3.14 and 3.07; R^3, 3.45 and 3.41. The resonances of $Me_2C{=\!=}NNMe_2$ hydrazone (in *trans*-$PdCl_2(Me_2C{=\!=}NNMe_2)_2$) follow: R^1, 3.01 and 3.12; R^3, 2.95 and 2.90. In the mixed complex, they are as follows: R^1, 2.45 and 2.98; R^3, 2.83 and 2.45.

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Received August 3, 1978

Formation of Metal Chelates in Secondary Ion Mass Spectrometry. Comparisons with Solution Chemistry

Sir:

We report a new area of application of secondary ion mass spectrometry (SIMS) in that metal chelates can be generated by ion bombardment of surfaces comprised of mixtures of metal salts and organic ligands. Some parallels with organometallic chemistry in solution will also be shown.

Organic molecules can be ionized by metal ion[1] or proton attachment[2] using a primary bombarding ion beam. Admixture of the organic compound (M) with a transition or alkali metal (C) salt is a particularly convenient method of cationizing organic molecules in SIMS.[3] The procedure yields molecular weight information (mass of the cationized molecule $(C + M)^+$), and a fragmentation pattern from which the molecular structure and, in some cases, the site of metal attachment can be inferred.

The possibility of forming gas-phase chelates in this way was tested by admixing 1,10-phenanthroline with $CoCl_2$, bom-

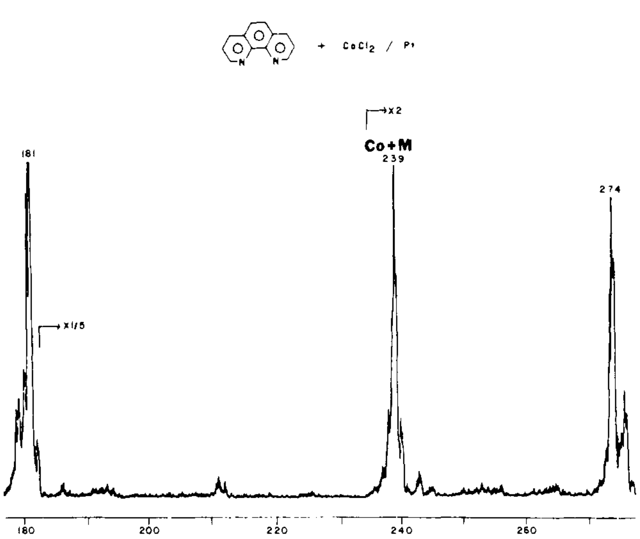

Figure 1. SIMS spectrum (partial) of 1,10-phenanthroline (M) mixed with $CoCl_2$ and supported on platinum showing (i) cationization, $(Co + M)^+$, *m/z* 239, (ii) attachment of a solvated cation to give *m/z* 274 $(CoCl + M)^+$, and (iii) protonation to yield *m/z* 181 $(H + M)^+$.

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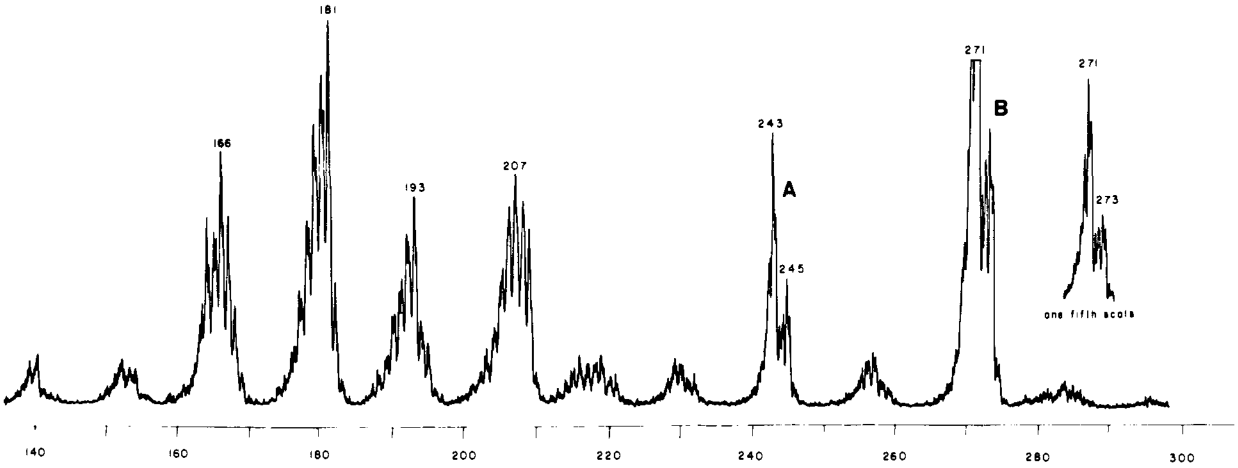

Figure 2. SIMS spectrum (partial) of a mixture of $CuCl_2$ with phenanthroline and dimethylphenanthroline showing copper attachment to both organic ligands. Peak A (*m/z* 243, 245) refers to the Cu^+/phenanthroline adduct, B (*m/z* 271, 273) to the Cu^+/dimethylphenanthroline adduct.

Table I. Chelation of Metals in SIMS: Ratio of Cationized $(C + M)^+$ to Ionized Molecules $(M^{+\cdot})$

chelate formed	$(C + M)^+/M^{+\cdot}$ (1,10-phenanthroline)	$(C + M)^+/M^{+\cdot}$ (2,9-dimethyl-phenanthroline)
$(Cu + M)^+$	215	290
$(Ni + M)^+$		100
$(Co + M)^+$	55	<0.1
$(Fe + M)^+$	160	<0.1
$(Cr + M)^+$	<0.1	<0.1
$(Zn + M)^+$	<0.1	
$(Cd + M)^+$	<0.1	

barding with Ar^+, and recording the SIMS spectrum.[4] This showed a prominent $(Co + M)^+$ ion at *m/z* 239 (Figure 1). It is noteworthy that the peak at *m/z* 180, corresponding to ionized phenanthroline, has a negligible intensity compared with that of its cationized analogue. This is an indication that the cationized species may be a stable gas-phase chelate, analogous in structure to that formed in solution.

The phenanthroline/$CoCl_2$ spectrum is also notable for the presence of an $(M + H)^+$ ion. The observation of both proton and transition metal ion attachment in the same spectrum suggests that the phenomena underlying both processes are similar.[5] Moreover, in other experiments, phenanthroline was observed to attach Fe^+ and Cu^+ (supplied as $FeCl_3$, $FeCl_2$, and $CuCl_2$) as well as Na^+ and K^+ present as impurities. In a competition study, phenanthroline was mixed with approximately equimolar amounts of $FeCl_3$, $CrCl_3$, $CuCl_2$, and $CoCl_2$. Intense peaks were observed (Table I) for the attachment of each metal except Cr,[6] even though Cr^+ was generated with comparable intensity with that of Fe^+ and was three times as intense as Co^+. Ion bombardment of mixtures of phenanthroline with $Zn(OAc)_2$ and $Cd(OAc)_2$ resulted in low ion yields for both the metal cation and the chelated organic.

For comparison with the 1,10-phenanthroline experiments, 2,9-dimethyl-1,10-phenanthroline was used as a ligand with the same metal salts. In aqueous solution the methyl groups cause steric hindrance between ligands, forcing tetrahedral coordination of the metal cation and giving 2,9-dimethyl-1,10-phenanthroline a selectivity for Cu(I) over the other transition metals. While there is no evidence that such a mechanism is operative in the SIMS experiments (see, however, ref 6), the observed attachment of metal cations does follow the same trend as in solution. In a competition experiment, dimethylphenanthroline was mixed with the chloride salts of Fe^{3+}, Co^{2+}, and Cu^{2+}, but, in contrast to to the analogous experiment using 1,10-phenanthroline, the SIMS spectrum showed only Cu^+ attachment. Another study of competition among Ni^{2+}, Na^+, and Cu^{2+} showed a small amount of Ni^+ attachment, the $(Ni + M)^+$ peak being ~15% of the total $(Cu + M)^+$ signal.

If the gas-phase organometallic species formed are indeed chelates, then the extra coordination sites of the central atom are unoccupied whereas solvent coordination occurs in solution. As a possible consequence, it was found that additional ligands were attached to the $(C + M)^+$ species in some cases. For example, the ion $(Fe + M + H_2O)^+$ was observed in the Fe/phenanthroline case and $(Co + M + Cl)^+$ in the $CoCl_2$/phenanthroline experiment.

Ion bombardment of the transition metal complex itself, rather than the ligand plus metal salt mixture, resulted in SIMS spectra characterized by a total absence of cationized molecules. The spectra show only low mass organic fragments and metal ions. The absence of metal ions chelated with intact organic ligands suggests that chelation occurs in the gas phase in the experiments with metal salts.

Figure 2 shows part of the SIMS spectrum of a mixture of 1,10-phenanthroline, 2,9-dimethylphenanthroline, and $CuCl_2$. This result illustrates the applicability of organic SIMS to mixtures. The different $(Cu + M)^+$:$M^{+\cdot}$ ratios for the two phenanthrolines are also noteworthy. The abundance of the cupriated species for dimethylphenanthroline is a factor of 6 larger than the molecular ion, whereas, for 1,10-phenanthroline, the $(Cu + M)^+$:$M^{+\cdot}$ ratio is only 0.8. Because both chelates originate from the same matrix and because the molecules can be expected to be ionized directly with comparable efficiencies, these differences must arise in the kinetics of chelate formation or dissociation. Dimethylphenanthroline is interpreted to form a more kinetically stable gas-phase copper complex than does 1,10-phenanthroline perhaps owing to steric inhibition of dissociation. This may be compared with solution behavior, in which a far larger *thermodynamic* stability constant is observed for the 1,10-phenanthroline-copper complex than for the complex with dimethylphenanthroline.[7,8]

SIMS provides a new avenue for the study of chelation of metals in otherwise inaccessible oxidation states and in the absence of solvent. These observations may also have application in chemical analysis. Use of a selective ligand allows the SIMS signal for a particular cation to be shifted out of the low mass region, where it may be subject to interferences. Trace analysis for a single cation in the presence of a complex matrix would appear to be facilitated.

Acknowledgment. This work was supported by the National Science Foundation, CHE 77-01295 and NSF-MRL DMR 76-00889A1.

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(4) Instrument parameters and sample preparation have been described (see ref 3 and H. Grade, M.S. Thesis, Purdue University, 1977). The organic compound was physically mixed with the metal salt(s) and the mixture burnished onto Pt foil. Samples ($\sim 1\ cm^2$) were bombarded with a 5-keV argon ion beam of 5×10^{-9} A at ~45° from the target normal. The vacuum chamber pressure remained between 5×10^{-9} and 2×10^{-8} Torr during the experiment.

(5) Our earlier studies[1,3] showed exclusive metal attachment whereas similar experiments[2] showed only protonation. Recent results by DeCorpo, et al. (R. J. Colton, J. S. Murday, J. R. Wyatt, and J. J. DeCorpo, paper presented at the 26th Annual Conference on Mass Spectrometry and Allied Topics, ASMS, St. Louis, Mo., 1978) show both protonation and metal attachment.

(6) Masses above $(C + M)^+$ suggest that the observed ions may arise, at least in part, from dissociation of the bis(tetradentate) species $(C + 2M)^+$

(7) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5237 (1962).

(8) Factors such as ligand field stabilization energies, oxidation states, and sputter yields must be considered in attempting to explain ion intensities of the different chelated metals. We believe that the chelates form just above the surface by the reaction $C^+ + M \rightarrow (C + M)^+$. This mechanism seems to be consistent with our earlier results[3] and with dynamic calculations of SIMS sputtering.[9]

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Received August 13, 1978

Ionization of Quaternary Nitrogen Compounds by Secondary Ion Mass Spectrometry

Sir:

Previously used primarily for analysis of metals, the technique of secondary ion mass spectrometry (SIMS) has recently emerged as an ionization method for studying organic compounds.[1] Earlier work from this laboratory reported the cationization of organic molecules by metals and the resulting fragmentation observed from the parent organometallic ion.[2] Reported here are studies of the direct ionization of quaternary ammonium salts which requires no cationizing metal. Previous work has shown that ammonium salts may be analyzed by field desorption.[3] This report on the direct ionization of quaternary ammonium salts via SIMS further extends the phenomenological similarities between the two techniques. These include the use of alkali metal attachment in both FD and SIMS.[4]

The SIMS spectrum[5] of $N(CH_3)_4Cl$ on Pt shows emission of the intact quaternary ammonium ion (*m/e* 74) as the most intense ion above *m/z* 30. Fragment ions were observed corresponding to loss of one and two molecules of methane to yield *m/z* 58 and 42 with relative abundances of 80 and 90%, respectively. Hence, the SIMS spectrum contains information on both the molecular weight and the structure of the quaternary ammonium salt. The salts *N*-methylpyridinium iodide, *N*-methyl-2,2′-bipyridinium iodide, and *N*-methylphenanthrolinium iodide all gave spectra in which the intact organic cations were the most abundant high mass ions.

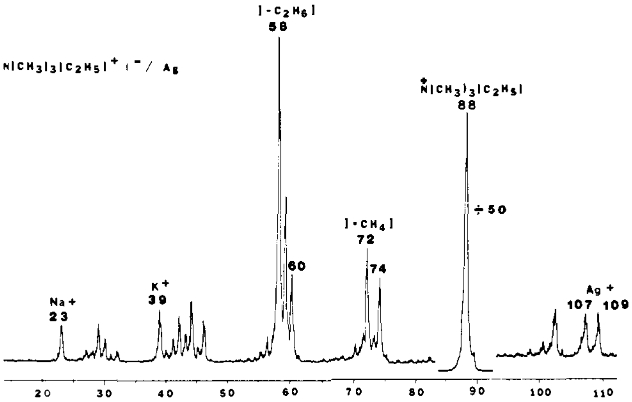

Figure 1. SIMS spectrum of ethyl trimethylammonium iodide showing emission of the intact cation and its characteristic fragmentation pattern.

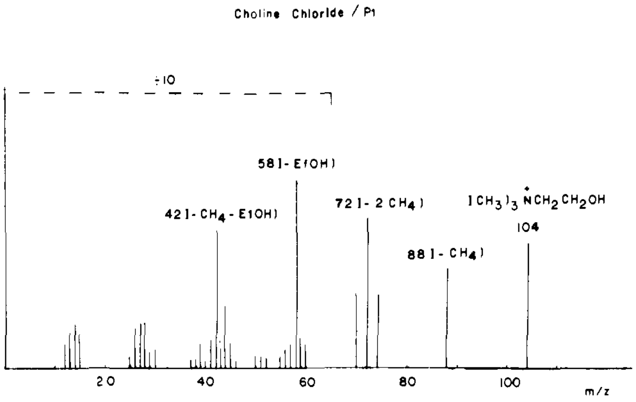

Figure 2. SIMS spectrum of choline chloride.

The spectrum of ethyltrimethylammonium iodide (Figure 1) was obtained in order to investigate the ionization mechanism. The base peak at *m/z* 88 corresponds to the intact quaternary ammonium ion. The virtual absence of exchange of methyl and ethyl groups indicates that emission of the cation occurs directly from the solid phase. This result excludes both emission from a plasma and ion formation via a gas-phase reaction of tertiary amine with alkyl iodide. Either of these alternatives would have resulted in formation of far larger amounts of $N(CH_3)_4^+$ and $N(CH_3)_2(C_2H_5)_2^+$ than were observed. A ratio of $N(CH_3)_2(C_2H_5)_2^+$ to $N(CH_3)_3(C_2H_5)^+$ to $N(CH_3)_4^+$ of 10:3:3 was expected for complete randomization. The observed ratio of 1:100:2 is only consistent with emission directly from the solid phase as the major ionization mechanism.[7]

To further test this mechanism a mixture of *N*-methylpyridinium iodide and its d_3 analogue (methyl deuterated) was examined. Both the d_0 and d_3 analogues of the intact cations were observed. Cations with one or two deuteriums would be expected should intermolecular hydrogen exchange occur, but such species did not appear in the SIMS spectrum. Apparently no significant intramolecular hydrogen exchange occurs, either, since only $CH_3\cdot$ and $CD_3\cdot$ losses were observed. These results support the direct cation emission mechanism.

Fragmentation patterns observed in the SIMS spectra parallel those determined for even-electron ions in the gas phase. In particular, Levsen and co-workers have studied the collision-induced dissociation of quaternary ammonium salts.[8] They observe elimination of alkane molecules and alkyl radicals from these species. These are exactly the processes seen in SIMS spectra, e.g., the methane losses from the tetramethylammonium ion discussed above. Similarly, *N*-methylbipyridinium iodide gives abundant fragments 92^+ and 78^+ corresponding to cleavage between the rings with and without hydrogen transfer, respectively.

A feature of these spectra is the occurrence of low abundance peaks corresponding to ions in which a hydrogen atom of the quaternary has been substituted by a halogen. This is evident from the spectrum of tetramethylammonium iodide which showed an abundant ion corresponding to iodine substitution for a hydrogen atom in the intact cation. A related

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