Analysis of Transition-Metal Compounds Containing Tetrathiafulvalene Phosphine Ligands by Fast Atom Bombardment Mass Spectrometry: Limitations and the Development of Matrix Additives for the Desorption of Multiply Charged Complexes

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A series of new complexes incorporating the functionalized tetrathiafulvalene (TTF) ligands *ortho*-$(CH_3)_2(P(C_6H_5)_2)_2$-TTF (*o*-P2) and $(P(C_6H_5)_2)_4$TTF (P4) have been prepared and studied by fast atom bombardment mass spectrometry (FABMS). The mononuclear *o*-P2 complexes $[M(o\text{-P2})_2](BF_4)_2$ (M = Fe, Pd, Pt) and $[Co(o\text{-P2})_2(NCCH_3)_2](BF_4)_2$ were synthesized from reactions of the free ligand with the fully solvated BF_4^- salts $[M(NCCH_3)_n](BF_4)_2$ (M = Fe, Co, n = 6; M = Pd, Pt, n = 4). The dinuclear P4 complex, $[Pt_2(P4)(NCCH_3)_4](BF_4)_4$, was produced by reacting the free ligand with $PtCl_2(NC_7H_5)_2$ followed by abstraction of the chlorides with $AgBF_4$ in acetonitrile. Reaction of $[Pd(NCCH_3)](BF_4)_2$ with 1 equiv of P4 produces the polynuclear compound formulated as $[Pd(P4)]_n(BF_4)_{2n}$ which was characterized by infrared, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopies and elemental analysis. The use of FABMS in this study was undertaken in order to elucidate the chemical options of multiply charged cations in the desorption process from the liquid matrix to the gas phase. The use of additives to the FAB matrix (*m*-nitrobenzyl alcohol) was demonstrated for the P4 complexes which do not give spectra in this medium due to a high positive net charge. The addition of triflic acid (HOTf or CF_3SO_3H) to the FAB matrix/analyte solution was shown to assist in the MS analysis of cationic complexes with up to six charges and a mass range up to *m/z* 4000. When HOTf is added, bound OTf^- anions are formed and are attached to the cationic complex, lowering the net charge to +1. The method of using matrix additives as opposed to chemically synthesizing the OTf^- compounds is a convenient in situ method which produces species that are capable of being analyzed by FABMS.

Introduction

The design of molecule-based materials with tunable conducting, optical, and magnetic materials is the focus of much research activity in synthetic organic and inorganic chemistry.[1,2] In one approach to preparing materials with paramagnetic metal centers in the same structural framework as open-shell π-organic radical cations, researchers are investigating salts of tetrathiafulvalene (TTF)-based radical cations with high-moment metal cluster anions.[3] Organic donor molecules such as TTF, bis-(ethylenedithio) tetrathiafulvalene (BEDT-TTF), and tetramethyltetraselenafulvalene (TMTSF) form salts with polychalcogenide, halide, and mixed chalcogenide/halide cluster anions of Re with remarkable variations in properties, differences that have been attributed to changes in the size, shape, and redox properties of the organic donor and inorganic acceptors.

An entirely different philosophy for the construction of hybrid inorganic/organic arrays involves the direct coordination of metals to organic radicals through a heteroatom.[4] In this vein, it has been shown that the use of open-shell oxygen donor ligands such as semiquinones,[5] nitroxides, and nitronyl nitroxides[6,7] contribute interesting variations to the electronic and magnetic properties of a metal-containing chain. The groups of Batail and Fourmigué et al. first demonstrated in 1992 the synthesis of a series of molecules such as 3,4-bis(diphenylphosphino)-3',4'-dimethyltetrathiafulvalene (*o*-P2) and tetra(diphe-

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nylphosphino)tetrathiafulvalene (P4).[1a,8] This series comprises stable redox-active ligands that form strong metal interactions enhanced by chelation through their phosphine functionalization. Work in our laboratories has established that cationic complexes of the type [M(*o*-P2)$_2$]$^{2+}$ and [M(P4)]$_n^{2n+}$ can be prepared by reactions of the solvated precursors [M(NCCH$_3$)$_{4-6}$]$^{2+}$ with the appropriate phosphine ligand.

In lieu of X-ray structures, a convenient tool for the characterization of these molecules, particularly with respect to nuclearity, is desired. Mass spectrometry techniques provide such a tool for detailed structural analysis, with fast atom bombardment (FABMS) being the method of choice for the analysis of nonvolatile, thermally labile compounds with molecular weights in the 500−3000 range.[9] However, approaches used for obtaining and interpreting mass spectra for organometallic complexes are not nearly as developed as those for organic molecules. For organic molecules, atom bombardment of a matrix/analyte solution typically yields protonated analytes as the most abundant species due to "desorption/ionization". If the species present in solution is already ionic such as Na$^+$ or K$^+$, the species need only be desorbed. In most cases, only singly charged ions are observed in FAB so the situation becomes more complex when an analyte in the matrix solution exists as a multiply charged species. The desorption of multiply charged transition-metal-containing species in FAB has long been recognized as a limitation of the experiment.[10] For organic molecules that are multiply charged anions in solution, matrix additives have been identified that assist analytes in lowering their net charge, to a single negative charge, during the desorption event.[11]

In the course of our studies on the tetrathiafulvalene phosphine complexes, we noted with interest, recent reports on the characterization of cationic "molecular squares". It appears that considerable promise exists for the use of FABMS to characterize cyclic inorganic ring structures with charges ranging from +4 to +8 when the counteranion is trifluoromethanesulfonate (triflate).[12] Given this precedence for the usefulness of the FABMS tool in these charged systems, considerations for the successful analysis of phosphine-containing cationic transition-metal species are presented here. The chemical options of highly charged ionic species in the FAB experiment will be considered. Specifically, metal-containing complexes of the form [M(*o*-P2)$_2$](BF$_4$)$_2$ will be evaluated. The mass spectrometric analyses are being developed simultaneously with synthetic protocols for these compounds. The goal of this work is to develop an understanding of the FAB mass spectra of such complexes and to identify approaches for obtaining structurally significant mass spectra. Also, the analysis of molecules containing the P4 ligand, such as [Pt$_2$(P4)(NCCH$_3$)$_4$](BF$_4$)$_4$, with a higher ionic charge in solution, will be discussed. The FAB spectrum of this, and of larger P4 complexes, will be considered

as well as a simple approach to obtaining meaningful spectra of multiply charged transition-metal species.

Experimental Section

Synthesis of *o*-P2 Complexes. The [M(*o*-P2)$_2$](BF$_4$)$_2$ (M = Pd, Pt, Fe) and [Co(*o*-P2)$_2$(NCCH$_3$)$_2$](BF$_4$)$_2$ complexes were synthesized by reacting 2 equiv of the *o*-P2 ligand, dissolved in 5 mL of CH$_2$Cl$_2$, with [M(NCCH$_3$)$_n$](BF$_4$)$_2$ (M = Pt, n = 4; M = Fe, Co, Pd, n = 6) dissolved in 5 mL of CH$_3$CN. The resulting solutions were stirred for 12 h, and the products were precipitated by the addition of toluene. This method is very similar to the previously reported synthesis of [Rh-(*o*-P2)$_2$](BF$_4$), which was structurally characterized by X-ray methods.[1a,b] All procedures for the iron complex were performed under anaerobic conditions, whereas the other metal products were handled in air. A more detailed example of these procedures is described as follows.

[Co(*o*-P2)$_2$(NCCH$_3$)$_2$](BF$_4$)$_2$. In separate flasks, 0.040 g (0.084 mmol) of [Co(NCCH$_3$)$_6$](BF$_4$)$_2$ was dissolved in 5 mL of acetonitrile, and 0.103 g (0.171 mmol) of *o*-(Ph$_2$P)$_2$Me$_2$TTF was dissolved in 5 mL of dichloromethane. The cobalt solution was added to the TTF solution, which effected a color change to dark brown, and the reaction solution was stirred for 12 h. The solution volume was reduced by ~50%, treated with 20 mL of toluene to afford a brown solid, and filtered in air. The remaining brown solid was washed with toluene, 3 × 10 mL, to remove unreacted *o*-P2 and with diethyl ether, 4 × 5 mL, until the washings became colorless. Finally, the solid was dried in vacuo. The yield was 0.098 g (77%).

[Pt$_2$(P4)(NCCH$_3$)$_4$](BF$_4$)$_4$. One equivalent of the P4 ligand and 2 equiv of PtCl$_2$(NC$_7$H$_5$)$_2$ were combined in CH$_2$Cl$_2$ to form the insoluble complex Pt$_2$(P4)Cl$_4$. The solid was then treated with 4 equiv of AgBF$_4$, and in CH$_3$CN, refluxed for 2 days. The resulting mixture was filtered to remove the AgCl byproduct, and the desired product was precipitated from solution with diethyl ether.

[Pd(P4)]$_n$(BF$_4$)$_{2n}$. Solid samples of P4 (0.207 g, 0.213 mmol) and [Pd(NCCH$_3$)$_6$](BF$_4$)$_2$ (0.116 g, 0.261 mmol) were loaded into separate flasks and dissolved in 6 mL of CH$_2$Cl$_2$ and CH$_3$CN, respectively. The P4 solution was then added to the metal solution, and the resulting mixture was stirred for 12 h, resulting in a dark brown solution. The solution was concentrated to 5 mL, treated with 20 mL of diethyl ether to yield a brown precipitate, and removed by cannula. The resulting brown solid was washed with diethyl ether 3 × 10 mL, and dried in vacuo. The yield was 0.243 g (91% based on [Pd(P4)][BF$_4$]$_2$). Anal. Calcd for PdP$_4$S$_8$C$_{54}$H$_{40}$B$_2$F$_8$: C, 53.12; H, 3.31. Found: C, 53.67; H, 3.69. ^{31}P{^{1}H} (δ ppm CD$_3$CN): 44.2. IR (Nujol, cm^{-1}): 1049 (ν_{B-F}), 689 (*o*-P2).

Mass Spectrometry. Mass spectra were obtained on a JEOL HX-110 double-focusing mass spectrometer (JEOL, Ltd., Tokyo, Japan) operated in the positive ion mode. Ions were produced by fast atom bombardment (FAB) with a beam of 6 kV Xe atoms and an emission current of 5 mA. The mass spectrometer was operated with an accelerating voltage of 10 kV at resolutions between 1500 and 3000. In the experiments investigating the desorption of Ba^{2+}, the solution used was BaCl$_2$ (EM Science, Gibbstown, NJ) dissolved in methanol (J. T. Baker, Phillipsburg, NJ) at a concentration of 5 nmol/μL. One microliter of analyte was mixed with 1 μL of glycerol (Sigma Chemical Co., St. Louis, MO) matrix on the FAB direct insertion probe, and spectra were obtained. The *o*-P2 and P4 metal complexes were dissolved in acetonitrile (J. T. Baker, Phillipsburg, NJ) at concentrations of 5 nmol/μL; 1 μL of this solution was mixed with 1 μL of *m*-nitrobenzyl alcohol (Aldrich Chemical Co., Milwaukee, WI) and introduced into the FAB ion source. Volatile solvents quickly evaporate and are removed when the target is placed into the vacuum system of the mass spectrometer. For the BaCl$_2$ and *o*-P2 complexes, mass spectra were obtained by scanning over the *m/z* range of 1−1500 Da in 15 s; for the P4 complexes, the *m/z* range of 1−6000 was scanned in 1 min. Multiple spectra were collected. In some experiments triflic acid was added; 1 μL of triflic acid (Eastman Kodak Co., Rochester, NY) was mixed with the analyte/matrix solution immediately prior to analysis.

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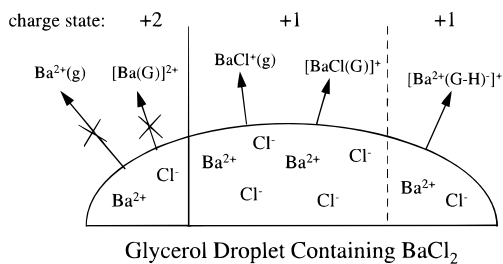
Figure 1. Desorption/ionization possibilities for Ba^{2+} from $BaCl_2$ in glycerol by +FAB.

Results and Discussion

A. FAB Mass Spectra of Species That Are Multiply-Charged in Solution. To consider the options of multiply charged ionic species in the FAB experiment, we will discuss $BaCl_2$ as an analyte using glycerol (G) as the matrix. As a solvent, glycerol is in many ways similar to water,[13] and $BaCl_2$ exists in ionic form in this matrix. A variety of desorption pathways yielding positive ions are shown in Figure 1. The formation of doubly charged ions, either bare, $[Ba^{2+}](g)$, or partially solvated, $[Ba^{2+}+G](g)$, is not expected. In FAB, insufficient energy is provided to condensed phase species to result in desorption of multiply charged ions. Ionic desolvation energies are proportional to the square of the ionic charge, according to the Born equation.[14] The Born equation was developed to estimate solvation energies of atomic and small molecular ions. A form of the equation, to describe the energy required for ion desolvation during desorption, is shown in eq 1.

$$\Delta_{desolv}G^{\circ} = +\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i}\left(1 - \frac{1}{\epsilon_r}\right) \qquad (1)$$

In eq 1, an ion of charge $z_i e$ and radius r_i is considered, being desorbed from a solution with a dielectric constant of ϵ_r, where ϵ_0 is the permittivity of a vacuum. The dielectric constant for glycerol is 42.5. The energy required for the complete desolvation of a Ba^{2+} ion from glycerol is 20.98 eV. The maximum energy available for molecular desorption in FAB has been estimated to be no greater than 19.9 eV.[15] Thus, one would not expect to form $Ba^{2+}(g)$ in the FAB experiment, for introduction into the mass analyzer, although it is the only form of barium that exists in the solution. If barium existed as Ba^+ in solution, only 4.6 eV would be required for its desolvation/desorption. Thus, singly charged species such as Na^+ are readily desorbed; multiply charged ions usually cannot be desorbed directly upon fast atom bombardment of a solution containing the ion. As will be seen in subsequent spectra, +2 ions can be desorbed in some cases. When charge is distributed throughout a molecular framework, the Born equation does not accurately represent solvation energies. However, for similar species, solvation energies will have a strong dependence on overall charge.

Figure 2 shows the +FAB mass spectrum of $BaCl_2$, using a glycerol matrix. Barium contains seven isotopes, in the range $^{130}Ba \rightarrow ^{138}Ba$. The most abundant form is ^{138}Ba, with a natural abundance of 71.6%. Each of the other isotopes has an abundance of less than 15%. If formed, $Ba^{2+}(g)$ ions would appear in the spectrum with an m/z value of 138/2 = 69; none
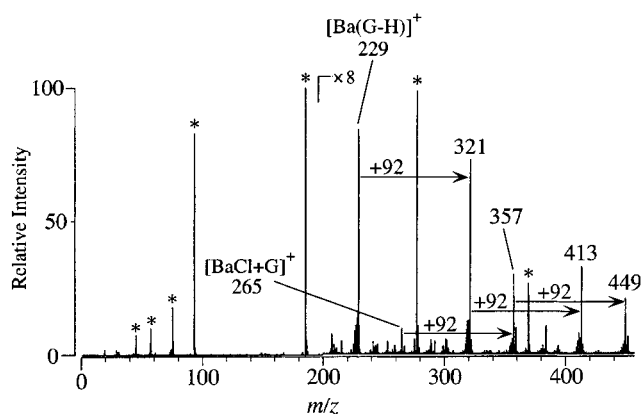

Figure 2. +FAB mass spectrum of $BaCl_2$ in glycerol. Peaks representing ions evolving from the glycerol matrix are labeled with an asterisk (*).

are observed. Also, no peak representing $Ba^+(g)$ is present (m/z = 138). Thus, reduction accompanying desorption, to lower the charge on the metal, does not occur. Typical of a FAB spectrum, most of the low-mass ions (below m/z = 200) are related to the glycerol matrix. The peaks at m/z = 93, 185, 277, 369, and 461 are all proton-bound glycerol clusters, $[G_n + H]^+$, $n = 1 \rightarrow 5$. The peaks at lower mass (m/z = 45, 57, 75) are fragment ions of glycerol.[16]

Interestingly, two types of ions are generated during FAB of $BaCl_2$ in G. An intense peak is observed at m/z = 229, which is not due to the glycerol matrix. From its isotope pattern, it must contain one Ba atom, and it does not contain Cl. The ion must be singly charged since the separation between isotope peaks is 1 amu. The ion corresponds to $[Ba + 91]^+$. Since the mass of G is 92, the added mass of 91 Da must be (G − H)⁻, the glyceride ion. Therefore the major peak in the spectrum at m/z = 229 represents $[Ba^{2+}(G - H)^-]^+$. Apparently, Ba^{2+} reacts with a glycerol molecule to form a singly charged ion, leaving a proton in solution, as suggested by reaction 2. A bound glycerol molecule forms a negatively

$$[Ba^{2+} + G](solv) \xrightarrow{FAB} [Ba^{2+}(G - H)^-]^+(g) + H^+(solv) \qquad (2)$$
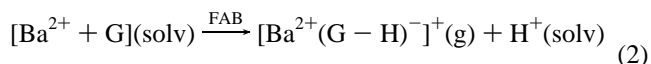
charged ligand (G − H)⁻, and the resulting complex has a single charge and can be desorbed. This is one example of the solution chemistry that may occur during the desorption process in order to reduce a high charge (greater than unity). Solvated forms of the m/z = 229 ion are observed at m/z = 321 and 413 in Figure 2. These three peaks are separated by 92 u, corresponding to the addition of neutral glycerol molecules.

If a Ba^{2+} ion reacts with G to form an anion and complexes with that anion to desorb with a single net charge, one would expect that the +2 metal ion could also bind to a Cl⁻ ion during desorption. A peak representing $BaCl^+$ (m/z = 173) is not observed. However, an ion is generated of the form $[BaCl + G]^+$ (m/z = 265), representing a solvated $BaCl^+$ ion. Since glycerol forms clusters with glycerol ions, clusters of glycerol attached to ions evolving from the $BaCl_2$ are not unexpected. In the FAB target in this experiment, $[Ba^{2+}] < [Cl^-] \ll [G]$, so it is not unreasonable that Ba^{2+} reacts with glycerol in solution as well as Cl⁻ in order to lower its charge. Similar systems have been studied by Miller.[17] Instead of describing the m/z = 265 ion as a solvated $BaCl^+$ species, it should be considered as

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Figure 3. Mononuclear structure M(*o*-P2)$_2^{2+}$.

an incompletely desolvated ion. Thus, its formation requires less energy than that for the completely desolvated form. Note that, similar to the sequence of peaks labeled $m/z = 229$, 321, and 413, addition of 1 and 2 G's to $m/z = 265$ occurs, leading to $m/z = 357$ and 449.

If cations from ionic compounds of the form $[M^{n+}(L^-)_n]$ have available pathways, they can desorb from solution with a low (single) charge in the positive ion FAB experiment. If they cannot, no analyte-related peaks will be observed in the +FAB spectrum. When analyzing an ionic compound by FAB, the chemist should not expect to detect abundant doubly or triply charged ions, although doubly charged ions are observed for some complexes.[10,18] Even in cases where doubly charged ions are observed, the singly charged ion peaks are usually of greater intensity with a better signal-to-noise (S/N) ratio. Observation of triply charged ions by FAB is extremely rare for ionic species.[19]

B. FAB Mass Spectra of [M(*o*-P2)$_2$](BF$_4$)$_2$ Complexes. 1. Choice of Matrix. While BaCl$_2$, in the example above, is soluble in glycerol, the *o*-P2 complexes studied here are not. A matrix used very successfully in the analysis of inorganic and organometallic compounds by FABMS is *m*-nitrobenzyl alcohol (NBA).[10,20,21] These complexes are soluble in this matrix, and representative ions are generated. There is a significant difference between NBA and glycerol in the FAB experiment. NBA is known to participate in redox reactions and oxygen-transfer reactions with analyte molecules, rather than just acid/base chemistry. NBA has both oxidative and reductive capabilities.[21] This provides an opportunity to investigate other chemical options available to multiply charged complexes, to lower their charge during FAB.

2. FAB Mass Spectra of *o*-P2 Complexes. The BaCl$_2$ FAB example represents a simple system to show how a multiply charged atomic ion can be converted into a singly charged molecular gas-phase species. Of course, the situation changes for the FAB analysis of these complexes. There are reduced direct metal−solvent interactions due to the presence of the *o*-P2 ligands, and the counterions are molecular and more complex. Also, the NBA solvent offers other options for desorption of charged complexes in lower charged states. A set of complexes of the form M(*o*-P2)$_2^{2+}$ was made (M = Fe^{2+}, Co^{2+}, Pd^{2+}, Pt^{2+}) and isolated as the tetrafluoroborate salts. The structure of the M(*o*-P2)$_2^{2+}$ complex is shown in Figure 3. Since the ligands are neutral, the metal determines the charge on the complex.

a. The FAB Mass Spectrum of [Fe(*o*-P2)$_2$](BF$_4$)$_2$. Figure 4a shows the +FAB spectrum of [Fe(*o*-P2)$_2$](BF$_4$) using NBA

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Figure 4. (a) +FAB mass spectrum of [Fe(*o*-P2)$_2$](BF$_4$)$_2$ in *m*-nitrobenzyl alcohol. (b) Enlargement of a portion of the mass spectrum about the $m/z = 1275$ peak. (c) Theoretical isotopic distribution for an ion with the [Fe(*o*-P2)$_2$ + F]$^+$ composition. Portions of the spectra are enlarged−multiplication factors are indicated (in these and other spectra).

as the matrix. All ions observed are +1 ions; no peak at $m/z = 628$, representing the doubly charged, intact Fe(*o*-P2)$_2^{2+}$ species, is observed. The most intense peak observed representing ions containing the intact Fe(*o*-P2)$_2$ core is at $m/z = 1275$. This is 19 u greater than the core mass and represents [Fe(*o*-P2)$_2$ + F]$^+$. Figure 4b shows an enlargement of the $m/z = 1275$ peak. The elemental composition of the ions represented by this peak is FeC$_{64}$H$_{52}$P$_4$S$_8$F. If the lowest mass isotope of each atom is used, 1273 would be the nominal mass. This peak is very small. The most intense peak in the isotopic distribution, $m/z = 1275$, will be used to represent [Fe(*o*-P2)$_2$ + F]$^+$. Figure 4c shows the theoretical isotopic distribution for this elemental composition as calculated by Isotopic Profiler from WindowChem Software, Inc. (Fairfield, CA). The ^{31}P-$\{^1$H$\}$ NMR spectrum of [Fe(*o*-P2)$_2$](BF$_4$)$_2$ displays two signals at $\delta = 56.1$ and 75.5 ppm, respectively, indicating the presence of two different phosphorus-containing species in solution. The resonance at 56.1 ppm is shifted downfield from the free ligand and falls in the range previously reported for M(*o*-P2)$_2$ complexes.[8a,1a] The second resonance is shifted ~20 ppm

downfield from the first, which has been reported by others to signify the presence of coordinated BF_4^- or F^- ligands.[22a-c] The ^{19}F NMR spectrum is in accord with this hypothesis, with singlets appearing at $\delta = -148.6$ and -503.0 ppm, respectively. The resonance at $\delta = -148.6$ ppm is in the range for values reported for uncoordinated BF_4^- and for the terminal fluorines of a coordinated BF_4^- anion.[22d] The singlet at -503.0 ppm is indicative of bound fluorine from coordinated BF_4^- or an abstracted F^- ion.[22b,e] In any case, it is obvious that the cation is associated with a F source in some form, which leads to a fluoride ion being associated with the expected $Fe(o\text{-}P2)_2^{2+}$ complex, reaction 3. Such a phenomenon has been seen

$$Fe(o\text{-}P2)_2{}^{2+} + BF_4{}^- \xrightarrow{\text{FAB}} [Fe(o\text{-}P2)_2 + F]^+ + BF_3(g) \quad (3)$$
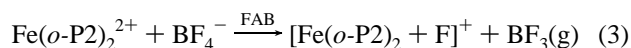
previously in the detection of $[LW(CO)_n(NO)F]^+$ ($n = 0, 1, 2$) ions in the mass spectra of $[LW(CO)(NO)SbF_6]^+$ (L = PMe_3, PMe_2PhP).[22b] This shows an additional option that multiply charged cations have, when the counterion is molecular and bonds within the counterion can be broken. With both F-coordinated and uncoordinated species present prior to analysis, it may be important to determine if correlations exist between the relative intensity of the $m/z = 1275$ peak and variations in the synthetic procedures. Figure 4a also shows a singly charged ion, $Fe(o\text{-}P2)_2^+$, at $m/z = 1256$. Apparently, in NBA, a $1e^-$ reduction of the complex occurs, either prior to or during the FAB process, to generate a singly charged ion.

Interestingly, the most intense analyte-related peak for this complex is $m/z = 600$ which represents the ionized free ligand, $o\text{-}P2^{\bullet+}$. Free $o\text{-}P2$ ligand could have been present in the sample, and the ion could have been formed directly. However, the complex was washed several times in order to remove any free ligand present, so it is unlikely that $o\text{-}P2$ was in the sample. The absence of a peak at -18.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum confirms this result. The other option is that the peak at $m/z = 600$ is a fragment ion. If the primary ion, $Fe(o\text{-}P2)_2^{2+}$, was desorbed but was unstable in the gas phase, fragments may appear at $m/z = 656$ and $m/z = 600$ representing $Fe(o\text{-}P2)^+$ and $o\text{-}P2^{\bullet+}$, respectively. However, $Fe(o\text{-}P2)^+$ is not observed. In a complex such as $Fe(o\text{-}P2)_2^{2+}$, considerable charge delocalization would be expected, and the formation of charged ligands during metal−ligand bond cleavage is reasonable. It is expected that the $o\text{-}P2$ ligand is easily ionized, due to the presence of the aromatic groups. For example, while the ionization energy (IE) of phosphine is 9.9 eV, the IE of triphenyl phosphine is more than 2 eV lower, 7.4 eV.[23] Thus, formation of ionized $o\text{-}P2$ ligands in the spectra should not be unexpected.

There are a number of other analyte-related peaks in the $m/z = 600-700$ region of the spectrum shown in Figure 4a. The peaks at $m/z = 616$ and 632 represent the addition of 1 and 2 oxygen atoms to the ligand. The oxidation sites are presumably at the phosphorus atoms since the $o\text{-}P2$ molecule appears to be capable of incorporating no more than 2 oxygen atoms. Also, +FAB spectra (not shown) of the free $o\text{-}P2$ ligand have been obtained and show the same two oxidation products. The peaks at $m/z = 616$ and 632 may arise from oxidation of the ligand

when it is still bound to the metal. Clearly, P-oxidation occurs at the expense of P−M complexation. This has been seen previously through the isolation of dioxidized P4 as a result of the reaction between $CoCl_2$ and P4.[8e] Other small peaks are present which show that the intact complex can undergo oxidation. For example, the peak at $m/z = 1291$, 16 u above 1275, represents $[Fe(o\text{-}P2)_2F + O]^+$. This should be more accurately described as $[Fe^{2+}(o\text{-}P2)(o\text{-}P2+O) + F^-]^+$. Finally, consider the peak at $m/z = 675$, which is 75 u above that for the free ligand. This corresponds to addition of an iron and a fluorine. This is the only peak which represents the metal with a single ligand attached, as $[Fe(o\text{-}P2)+F]^+$.

The $BaCl_2$ example showed that multiply charged metals have a variety of options in generating singly charged species in the desorption process. The $[Fe(o\text{-}P2)_2](BF_4)_2$ data show that additional options are available when the counterion is BF_4^-. In this case, the spectrum is dominated by ions representing the free ligand, and relatively small peaks establish the molecular structure.

b. The FAB Mass Spectrum of $[Pt(o\text{-}P2)_2](BF_4)_2$. On the basis of the spectrum of the $Fe(o\text{-}P2)_2^{2+}$ complex, we would expect certain peaks to be observed for the platinum complex. Few of these are present in the spectrum, which is shown in Figure 5a. On the basis of data obtained using $Fe(o\text{-}P2)_2^{2+}$, one would expect no peak for the doubly charged $Pt(o\text{-}P2)_2^{2+}$ ion ($m/z = 698$). The spectrum shown in Figure 5a displays a relatively intense peak at $m/z = 698$. Isotopic peaks for the doubly charged ion displayed a separation of 0.5 m/z units between peaks and an oxygen adduct ($m/z = 706$) at only 8 m/z units higher than the peaks for $Pt(o\text{-}P2)_2^{2+}$, confirming the desorption of doubly charged ions. In contrast to the spectrum of the iron complex, no peak representing the ionized $o\text{-}P2$ ligand is present at $m/z = 600$. This may suggest that there is a metal-dependent relationship controlling the relative abundances of the $M(o\text{-}P2)_2^{2+}$ and $o\text{-}P2^{\bullet+}$ ions. The $M(o\text{-}P2)_2^{2+}$ species should have different charge distributions when M = Fe and Pt. The sum of the first and second ionization energies of Fe (24 eV) is less than that for Pt (27.5 eV).[24] Thus, the iron complex may have more $L^{\delta+}-M^+-L^{\delta+}$ character and the Pt complex more $L-M^{2+}-L$ character. Delocalized charge can weaken the metal−ligand interaction and would result in an ionized ligand during bond cleavage of the desolvated complex in the case of iron. If a larger fraction of the total charge resides on the metal in the platinum complex, then the $Pt(o\text{-}P2)_2^{2+}$ species may survive the desorption process, without undergoing fragmentation.

For the iron complex, a small peak was seen for $Fe(o\text{-}P2)_2^+$ due to a $1e^-$ reduction, possibly during the desorption process. Figure 5a shows that $Pt(o\text{-}P2)_2^+$ ($m/z = 1396$) is an intense peak in the spectrum. The second IE of Pt (18.6 eV) is greater than that of Fe (16.2 eV);[25] thus reduction by reaction with NBA is more exothermic for the Pt complex, favoring formation of the singly charged $Pt(o\text{-}P2)_2^+$ species. Figure 5, parts b and c, shows the isotopic peaks for $m/z = 1396$ and the theoretical isotopic distribution, confirming its elemental composition and its net charge.

The spectrum of the iron complex showed that the doubly charged species could react with BF_4^- to form a singly charged gas-phase species, via fluoride extraction. No ions are formed containing a Pt−F bond. There is, however, a peak at $m/z =$

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(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics and American Chemical Society: New York, 1988.

(24) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: New York, 1972.

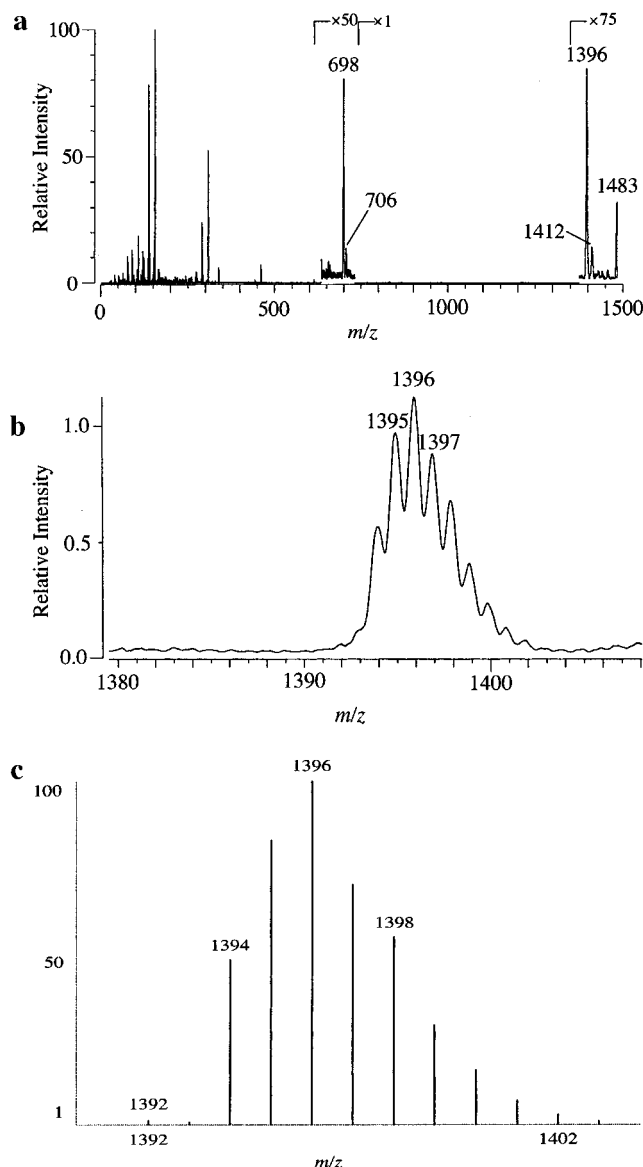(25) Miller, J. M.; Jones, T. R. B.; Deacon, G. B. *Inorgan. Chim. Acta* **1979**, *32*, L75.

Figure 5. (a) +FAB mass spectrum of $[Pt(o\text{-}P2)_2](BF_4)_2$ in *m*-nitrobenzyl alcohol. (b) Enlargement of a portion of the mass spectrum about the $m/z = 1396$ peak. (c) Theoretical isotopic distribution for an ion with the $Pt(o\text{-}P2)_2^+$ composition.

1483 which represents the addition of the BF_4^- anion, $[Pt(o\text{-}P2)_2 + BF_4]^+$, not unlike the complexation of Ba^{2+} with Cl^- to form a singly charged gas-phase species.

In the spectrum of the iron complex, evidence for oxidation was observed. The free ligand, as the mono- and di-oxide, was observed. Oxygen addition to the complex was also directly observed. In the spectrum of the Pt complex, there is a peak 16 u above $m/z = 1396$, representing oxygen addition to the singly charged complex. Thus, the ion with $m/z = 1412$ in Figure 5a is described as $[Pt(o\text{-}P2)(o\text{-}P2 + O)]^+$.

The complexes of $[Pt(o\text{-}P2)_2](BF_4)_2$ and $[Fe(o\text{-}P2)_2](BF_4)_2$ show that there is a strong metal dependence on the +FAB spectra of *o*-P2 complexes. Hard/soft acid/base (HSAB) theory may be a useful tool in predicting metal-dependent differences.[25] In reactions involving F^- extraction from BF_4^-, HSAB theory would suggest the process to be more likely for Fe than Pt; this is observed. Additional data for other metal complexes is provided in Table 1. The iron and cobalt complexes were the only ones observed to extract F^-, while the larger divalent metals form adducts with the intact BF_4^- ligand, supporting this correlation.

Table 1. Ion Intensities for $[M(o\text{-}P2)_2](BF_4)_2$ Complexes by +FAB[a]

metal	C^+	C^{2+}	$[C + O]^+$	$[C + F]^+$	$P2^{\bullet+}$	$M(o\text{-}P2)^+$	$[C + BF_4]^+$
Fe^{2+}	W		W	I	I		
Co^{2+}	I	M	W	W	W	W	
Pd^{2+}	I	M	W			M	M
Pt^{2+}	I	M	W				M

^{a} C = $[M(o\text{-}P2)_2]$. I = intense peak; M = medium intensity peak; W = low intensity peak.
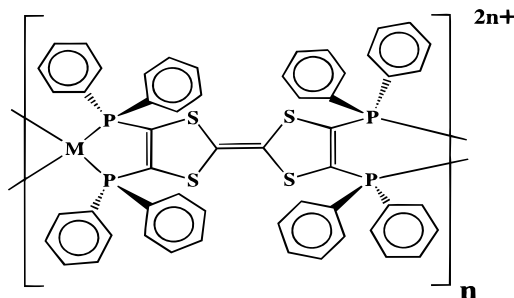
Figure 6. Polynuclear structure $[M(P4)]_n^{2n+}$.

The M-ligand bonds are more easily cleaved in the Fe complex than in the Pt complex, consistent with HSAB interactions. Again, the Pd complex yields a spectrum similar to that observed for Pt, from the data in Table 1. Table 1 also further supports the proposal that the intensity of the peak representing the ionized, free ligand is proportional to the sum of the first and second IEs of the metal. Of the four metals, the sum is lowest for Fe, and in Figure 4a the $o\text{-}P2^{\bullet+}$ peak is most intense. The sum is higher for Co, and a weak signal for the ionized ligand is observed; the sum is highest for Pt and Pd, and no ionized ligand peak is present.

C. FAB Mass Spectra of Transition-Metal Complexes of the P4 Ligand. Structurally similar to *o*-P2, the P4 ligands contain four phosphines. It is apparent that the use of P4 can lead to oligomeric complexes of the type $[M(P4)]_n^{2n+}$, Figure 6. These represent an important aspect of the analytical challenge of this work. Due to the unavailability of single crystals at this stage, it is unclear precisely what oligomeric species are being formed. Consequently, there is a keen interest in being able to identify them using FABMS. Unfortunately, with each additional metal, the charge increases by +2, and the complexes become increasingly refractory to FAB analysis, unless the species in solution can access chemical routes to sufficiently lower their charge during the desorption process. The work presented for the *o*-P2 complexes was undertaken in an attempt to develop an understanding of how the structures of such larger species correlate with the FAB spectra obtained.

1. The FAB Mass Spectrum of $[Pt_2(P4)(NCCH_3)_4](BF_4)_4$. The first P4 complex studied was $[Pt_2(P4)(NCCH_3)_4](BF_4)_4$, which was synthesized specifically to terminate with one P4 ligand and two metals (see Experimental Section). Each square-planar Pt^{2+} is also bound, initially, to two acetonitrile molecules, Figure 7. In solution, the core cationic complex is quadruply charged, $[Pt_2(P4)]^{4+}$. There is no evidence in the spectra that the acetonitrile ligands are retained. Figure 8a shows the +FAB spectrum of $[Pt_2(P4)](BF_4)_4$ using NBA as the matrix. Due to the high desolvation energy for this highly charged ion and the limited amount of energy provided by the fast atom beam, the ions must access a pathway to reduce their charge. It apparently cannot do so; desorption does not occur, and no gas-phase ions representing this complex, in any charge state, are formed.

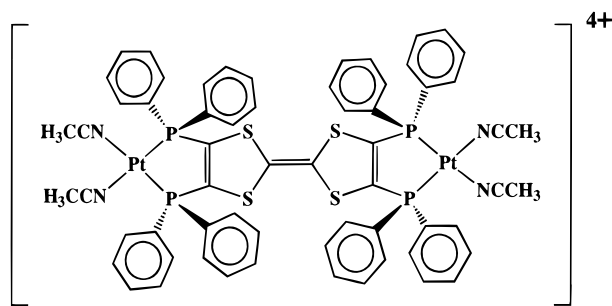In FAB, some analytes show a strong dependence on the matrix used. However, for organometallic and inorganic

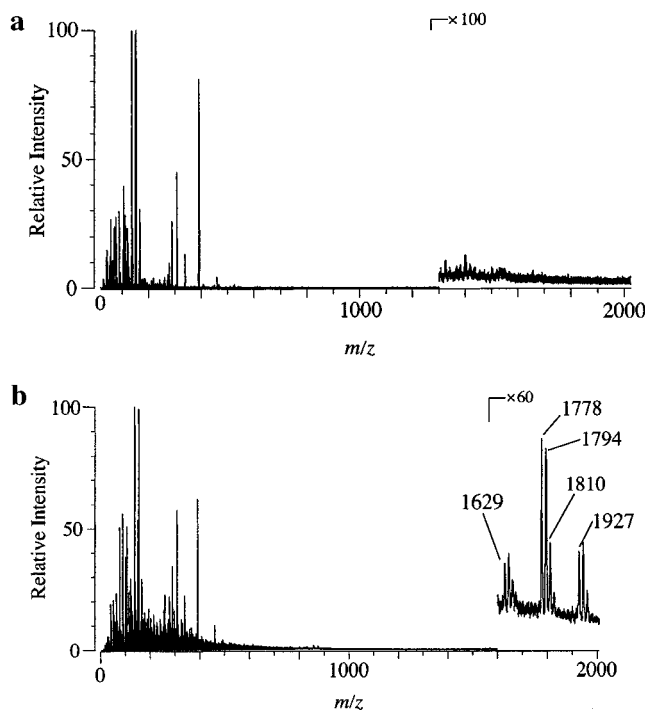**Figure 7.** Dinuclear structure $[Pt_2(P4)(NCCH_3)_4]^{4+}$.

Figure 8. +FAB mass spectrum of $[Pt_2(P4)(NCCH_3)_4](BF_4)_4$ in (a) *m*-nitrobenzyl alcohol and (b) *m*-nitrobenzyl alcohol with addition of triflic acid.

complexes, NBA is preferred. When organic molecules cannot be readily detected in FAB, "additives" can be used. These are frequently as simple as acids (to increase the amount of protonated molecules formed) or salts (to allow species such as $[M + Na]^+$ to be formed). In considering possible additives, we noted that some highly charged organometallic complexes have been successfully characterized by FAB.[12,26] For example, Stang et al.[12] used FAB to characterize a complex containing four Pt^{2+} ions, introduced as a $[core]^{8+}(L^-)_8$ salt. They observed singly charged species in the mass spectrum such as $[core^{8+} + 7L^-]^+$. Unfortunately, similar species are not formed in the $[Pt_2(P4)](BF_4)_4$ experiment. One possibly important variable is that, in the Stang experiment, the counteranion used was triflate ($CF_3SO_3^-$ or OTf^-). Rather than have the P4 compounds made again as the triflate salts, the decision was made to evaluate NaOTf as a matrix additive in these experiments. This approach did not assist in generating ions related to the $[Pt_2-(P4)]^{4+}$ complex. However, success was achieved by using triflic acid (HOTf) as a matrix additive.

D. HOTf as a Matrix Additive in FAB. When 1 μL of HOTf is added to the NBA matrix/analyte solution used to obtain the spectrum shown in Figure 8a, that shown in 8b is

obtained. High-mass ions in the $m/z = 1500-2000$ range are now observed. The mass of the $Pt_2(P4)^{4+}$ core is 1331 u (based on the most abundant isotope of the metal, ^{195}Pt). The most intense peak in Figure 8b in the expanded region of the spectrum is at $m/z = 1778$, which is 447 u greater than the core mass. Since triflic acid molecules have a mass of 150 u, this corresponds to the addition of three triflate ions, each with a mass of 149 u, reaction 4. That is, the addition of triflic acid

$$[Pt_2(P4)]^{4+} + 3HOTf]_{NBA} \xrightarrow{FAB} [Pt_2(P4)](OTf)_3^+(g) \quad (4)$$

allows for the detection of +4 species that were present in the NBA solution and that could not be successfully converted into lower-charged species without this additive. As previously reported, triflic acid does not serve as a source of fluoride ions, which explains why F^- abstraction was not observed.[27]

Oxygen adducts are seen at $m/z = 1794$, 1810, and 1826 with each peak representing $[Pt_2(P4)(OTf)_3+O]^+$, $[Pt_2(P4)(OTf)_3+2O]^+$, and $[Pt_2(P4)(OTf)_3+3O]^+$, respectively. Recall that, in the case of *o*-P2 complexes, no more than two oxygen atoms could be added. Other peaks in the spectrum include $m/z = 1629$, which represents $[Pt_2(P4)(OTf)_2]^+$, and a peak at $m/z = 1927$, which represents $[Pt_2(P4)(OTf)_4]^+$. Presumably, the $m/z = 1629$ peak is a partially reduced form, $[Pt^{2+}Pt^+(P4)(OTf)_2]^+$. Reduction of Pt^{2+} in the *o*-P2 complex was also observed. More interesting is the $m/z = 1927$ peak, which could represent a mixed valence species $[Pt^{2+}Pt^{3+}(P4)(OTf)_4]^+$. Oxidation of a Pt^{2+} would require a considerable amount of energy, even in a solvent in which oxidation has been reported to occur. A more reasonable possibility is that oxidation of the ligand has occurred to give $[Pt^{2+}Pt^{2+}(P4)^+(OTf)_4]^+$. In any case, the ion observed contains four triflates; the increased electrostatic interactions of the charged ligands with the charged metals may effectively stabilize the higher-charge state in this gas-phase complex. These results show that addition of triflic acid allows for the detection of ions present in the FAB matrix that are undetected in the normal FAB experiment.

To test the general utility of triflic acid addition, the oligomeric complex $[Pd(P4)]_n(BF_4)_{2n}$ was analyzed by FAB using NBA as the matrix. Again, no peaks representing the analyte are observed, Figure 9a. Triflic acid was then added to the matrix/analyte solution, and the spectrum shown in Figure 9b was obtained. In this case, ions with m/z values as large as 4000 were detected. When expanded, each peak in Figure 9b contains a cluster of peaks representing various oxygen-containing forms. For example, the peak at $m/z = 940$ represents the ionized P4 ligand. Higher mass peaks at $m/z = 956$, 972, 989, and 1015 indicate the addition of up to 4 oxygen atoms (1 to each phosphorus atom). The dominant peaks represent $[Pd(P4)](OTf)^+$ ($m/z = 1194$), $[Pd_2(P4)](OTf)_3^+$ ($m/z = 1601$), $[Pd_2(P4)_2](OTf)_3^+$ ($m/z = 2543$), $[Pd_3(P4)_2](OTf)_5^+$ ($m/z = 2945$), and $[Pd_3(P4)_3](OTf)_5^+$ ($m/z = 3890$). Clearly, reduction and triflate addition occurs to yield singly charged ions which are desorbed. The important result is the observation that an oligomeric mixture of complexes was formed with $n \geq 3$. Larger oligomers may be present but not detected. The P4 complexes could not have been characterized by FAB without the chemical assistance of an additive such as triflic acid.

Having demonstrated the utility of triflic acid addition, the question remains as to why it is effective in enhancing detection of highly charged species in the FAB experiment and why addition of sodium triflate is not. We will assume that, for the

(26) Didier, P.; Jacquet, L.; Mesmaeker, A. K.-D.; Hueber, R.; van Dorsselaer, A. *Inorg. Chem.* **1992**, *31*, 4803.

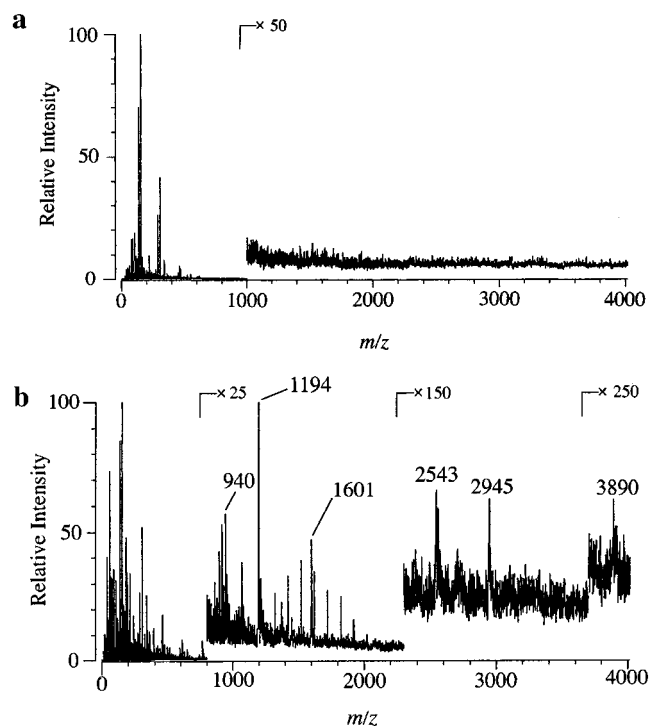(27) Stang, P. J.; White, M. R. *Aldrichimica Acta* **1983**, *16*, 15.

Figure 9. +FAB mass spectrum of $[Pd(P4)]_n(BF_4)_{2n}$ in (a) *m*-nitrobenzyl alcohol and (b) *m*-nitrobenzyl alcohol with addition of triflic acid.

amount of triflic acid used, the NBA solvent used, and the dielectric constant of NBA, most of the triflic acid is present as HOTf. We will also assume that one or more triflic acid molecules are present in the solvation sphere of ionic species formed. In the liquid FAB target, ions and their solvation spheres are more accurately described as $[Pt_2(P4)]^{4+}(NBA)_x(HOTf)_y$, for example. From such species, desorbed, desolvated ions are formed. In the desorbed species, whatever their final form, all NBA solvent molecules are removed; when HOTf is added, all are removed as well. However, the triflic acid appears to be converted into triflate ions during the atom bombardment process. The neutral triflic acid may easily bind to the core metal complex, while counteranions are solvated and are farther from the cations. Thus, when energy is deposited and desorption can occur, one or more triflic acids are converted into triflate ions, releasing protons to the solution, reaction 5, similar to the reaction of Ba^{2+} with glycerol.

$$[Pt_2(P4)]^{4+}(HOTf)_3(solv) \xrightarrow{FAB} [Pt_2(P4) + 3OTf^-]^+(g) + 3H^+(solv) \quad (5)$$
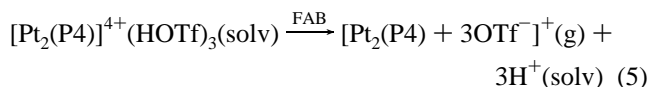
Conclusions

Mass spectrometry is a commonly used tool in the development of synthetic methodology in organic chemistry, since meaningful spectra can usually be obtained in the period of less than an hour. However, inorganic and organometallic chemists turn far less frequently to MS, in part because of the situation encountered in the analysis of the metal tetrathiafulvalene phosphine complexes described in this report. Highly charged states negate the possibility of generating analyte-related gas-phase species for subsequent mass spectrometric analysis. The conversion of multiply charged cationic complexes to singly charged species by acquiring anions from neutral molecules in the solvation sphere appears to be a viable pathway. For compounds that are soluble in glycerol, glycerate generation can occur, but when *m*-nitrobenzyl alcohol alone is used, the

analogous process does not occur. Triflic acid as an additive, however, seems to be able to serve in this capacity. The neutral HOTf molecule complexes with the multiply charged species, it forms an anionic ligand that strongly binds to the metal center(s), and it ejects a stable cation (proton) into the solution. Overall, the process can occur with the energy available in the FAB experiment. As synthetic procedures develop and larger oligomeric species of the tetraphosphine ligand (P4) in this work are generated, we will be in a position to determine the range of charge states over which FAB can be applied when matrix additives are employed.

It should be noted in closing that, while the work reported here used FAB, a variety of desorption/ionization techniques are now available in mass spectrometry. Newer methods such as electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) are rapidly becoming more available, while FAB continues to find new areas of application.[28] Each method has its strengths, weaknesses, successes, and failures, which is why few MS laboratories solve structural problems with just one technique. MALDI has captured the attention of the MS community by generating predominantly singly charged ions from analytes with molecular masses greater than 100 000. The role of additives in the MALDI experiment is not well-understood. In making the target for laser irradiation, matrix, analyte, and additives must first be cocrystallized. Triflic acid is not a candidate additive in MALDI, since it is a liquid at room temperature. Electrospray is an obvious method to turn to when the analyte is multiply charged in solution, since it is capable of generating multiply charged gas-phase ions. However the mass spectrometer of choice in ESIMS is usually a quadrupole mass filter or an ion trap. These have limited m/z ranges, relative to time-of-flight or magnetic sector instruments. Also, they do not provide high-resolution data as would a double-focusing instrument. There are advantages to using the FAB-based approach developed here, since singly charged forms of the analyte are generated. This facilitates the interpretation of MS/MS spectra which can provide structural information. While MS/MS spectra can be generated for multiply charged species, interpretation of the resulting spectrum can be very difficult. If a +4 ion is subjected to collisional-activation and fragmentation, it will typically form +4, +3, +2, and +1 fragment ions. This is particularly difficult to deal with when the analytes are metal-containing compounds such as those discussed here.

(28) Henry, C. *Anal. Chem.* **1997**, 625A.