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Fast Atom Bombardment Tandem Mass Spectrometry of (Polypyridyl)ruthenium(II) Complexes

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The mass spectra of some (polypyridyl)ruthenium(II) complexes of the type $[Ru_xL(bpy)_{2x}](PF_6)_{2x}$ (L = 2,2':6,2''-terpyridine (x = 1), 3,3':5,3''-bis(dimethylene)-2,2':6,2''-terpyridine (x = 1), 5,6,9,10,11,12,15,16-octahydrocycloocta[1'',2'':5,6;4'',3'':5',6']dipyrido[2,3-b:2',3'-b]di[1,10]phenanthroline (x = 1, 2), and N,N'-dimethylene-2,2'-biimidazole (x = 1; bpy = 2,2'-bipyridine) have been investigated by using fast atom bombardment tandem mass spectrometry. The low-energy collision-induced dissociation (CID) spectra provide confirmation of the structures and details about fragmentations of the complexes. The observed decomposition pathways involve losses of intact ligands, PF_6^- counterions, simple bond cleavages, fluoride transfers from the PF_6^- counterion to the Ru(II) center with loss of PF_5, and reductive eliminations of HF. The fluoride-transfer reaction can be used to determine the coordination of the chelating ligands in the parent complex.

Introduction

Ruthenium complexes containing 2,2'-bipyridine (bpy) ligands and related analogues have been the subject of recent investigations.[1-3] These compounds have promise for the conversion of solar power into electrical and chemical energy.[3-7] A variety of ruthenium complexes with ligands consisting of polyaza cavity-shaped macrocycles have been synthesized with the intent of inducing unusual metal complex chemistry and optimizing photocatalytic efficiency.[8-13]

Various analyses of Ru(II) complexes with polypyridine ligands have been reported. Others have investigated the resonance Raman spectra of various reduction products of tris(bipyridyl)-ruthenium(II).[14] Mass spectrometric techniques for the characterization of involatile, intractable organometallic complexes have been successfully developed, such as field desorption (FD) mass spectrometry,[15-17] electrohydrodynamic mass spectrometry (EHMS),[18] laser desorption mass spectrometry (LDMS),[19] secondary ion mass spectrometry (SIMS),[20,21] and fast atom bombardment (FAB) mass spectrometry.[17,22-24] In general, singly charged ions are produced by using these techniques. However, the observation of doubly charged ions from coordination compounds containing multiply charged cationic metal centers has been reported. Cook and co-workers have reported forming $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ using electrohydrodynamic mass spectrometry (EHMS).[18] Doubly charged ions, including $[Ru(bpy)_3]^{2+}$, from coordination compounds have also been observed in FAB mass spectra.[23,24] In addition, the mass spectra of coordination complexes have been compared with their properties in solution.[17,19] The FAB process can be an energetic ionization method leading to various rearrangements and recombinations.[25]

One of the challenges to be met in utilizing FAB mass spectra is to relate observed fragmentations to the structure of the organometallic complexes. Tandem mass spectrometry (MS/MS) has proven useful for the structural analysis and in studying dissociation pathways for various ions.[26,27] We report here the application of fast atom bombardment tandem mass spectrometry to the analysis of several Ru(II) complexes containing multidentate polypyridine ligands. These compounds, of the form $[Ru_xL(bpy)_{2x}](PF_6)_{2x}$ (L = 2,2':6,2''-terpyridine (x = 1), 3,3':5,3''-bis(dimethylene)-2,2':6,2''-terpyridine (x = 1), 5,6,9,10,11,12,15,16-octahydrocycloocta[1'',2'':5,6;4'',3'':5',6']dipyrido[2,3-b:2',3'-b]di[1,10]phenanthroline (x = 1, 2), and N,N'-dimethylene-2,2'-biimidazole (x = 1; bpy = 2,2'-bipyridine), have been investigated by using low-energy collision-induced dissociation to determine fragmentation pathways leading to various ions observed in the FAB mass spectra. The results presented here identify fragmentation channels and reactions that can be interpreted in terms of simple bond cleavages, ligand losses, ligand substitutions involving a fluoride transfer from the outer-sphere counterion to an inner-sphere coordination site on the Ru(II) center, and intramolecular oxidative addition with reductive elimination of HF.

(1) Watts, R. J. Ruthenium Polypyridyls. *J. Chem. Educ.* **1983**, *60*, 834–842.
(2) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*, Elsevier, New York, 1984; Chapter 9.
(3) Kalyanasundaram, K. Photophysics, Photochemistry and Solar Energy Conversion with Tris(bipyridyl)ruthenium(II) and its Analogues. *Coord. Chem. Rev.* **1982**, *46*, 159–244.
(4) Connolly, J. S. In *Photochemical Conversion and Storage of Solar Energy*; Academic: New York, 1981; Chapters 4 and 5.
(5) Abruña, H. D.; Teng, A. Y.; Samuels, G. J.; Meyer, T. J. Reduction of Water to Hydrogen by Reduced Polypyridine Complexes of Ruthenium. *J. Am. Chem. Soc.* **1979**, *101*, 6745–6746.
(6) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. Photochemistry of $Ru(bpy)_3^{2+}$. *J. Am. Chem. Soc.* **1982**, *104*, 4803–4810.
(7) Brewer, K. J.; Murphy, W. R., Jr.; Spurlin, S. R.; Petersen, J. D. The Next Generation of (Polyazine)ruthenium(II) Complexes. *Inorg. Chem.* **1986**, *25*, 882–884.
(8) Thummel, R. P.; Decloitre, Y. Polyaza Cavity-Shaped Molecules. 8. Ruthenium(II) Complexes with 3,3'-Annelated Derivatives of 2-(2'-Pyridyl)quinoline and 2-(2'-Pyridyl)-1,8-naphthyridine. *Inorg. Chim. Acta* **1987**, *128*, 245–249.
(9) Thummel, R. P.; Jahng, Y. Polyaza Cavity-Shaped Molecules. 9. Ruthenium(II) Complexes of Annelated Derivatives of 2,2':6,2''-Terpyridine and Related Systems: Synthesis, Properties, and Structure. *Inorg. Chem.* **1986**, *25*, 2528–2533.
(10) Thummel, R. P.; Lefoulon, F. Polyaza Cavity Shaped Molecules. 11. Ruthenium Complexes of Annelated 2,2'-Biquinoline and 2,2'-Bi-1,8-naphthyridine. *Inorg. Chem.* **1987**, *26*, 675–680.
(11) Thummel, R. P.; Lefoulon, F.; Korp, J. D. Polyzaza Cavity-Shaped Molecules. 12. Ruthenium(II) Complexes of 3,3'-Annelated 2,2'-Bipyridine: Synthesis, Properties, and Structure. *Inorg. Chem.* **1987**, *26*, 2370–2376.
(12) Thummel, R. P.; Lefoulon, F.; Chirayil, S. A. Ruthenium Tris(diimine) Complex with Three Different Ligands. *Inorg. Chem.* **1987**, *26*, 3072–3074.
(13) Thummel, R. P.; Hery, C.; Williamson, D.; Lefoulon, F. Polyaza Cavity Shaped Molecules. 15. Stereocontrol in the Formation of Binuclear Complexes. *J. Am. Chem. Soc.* **1988**, *110*, 7894–7896.
(14) Angel, S. M.; DeArmond, M. K.; Donohoe, R. J.; Hanck, K. W.; Wertz, D. W. Resonance Raman Spectra of the First Three Reduction Products of Tris(bipyridyl)ruthenium(II). *J. Am. Chem. Soc.* **1984**, *106*, 3688–3689.
(15) Games, D. E.; Gower, J. L.; Gower, M.; Kane-Maguire, L. A. Field Desorption Mass Spectrometry of Neutral π-Hydrocarbon Organometallic Complexes. *J. Organomet. Chem.* **1980**, *193*, 229–234.
(16) Games, D. E.; Gower, J. L.; Kane-Maguire, L. A. Characterization of Cationic Coordination Complexes using Field Desorption Mass Spectrometry. *J. Chem. Soc., Dalton Trans.* **1981**, 1994–1996.
(17) Cerny, R. L.; Sullivan, B. P.; Bursey, M. M.; Meyer, T. J. Fast Atom Bombardment and Field Desorption Mass Spectrometry of Organometallic Derivatives of Ruthenium(II) and Osmium(II). *Inorg. Chem.* **1985**, *24*, 397–401.
(18) Chan, K. W. S.; Cook, K. D. Factors Affecting Mass Spectral Sensitivity for Ions Sampled by Field Evaporation from a Liquid Matrix. *Anal. Chem.* **1983**, *55*, 1306–1309.
(19) Balasanmugam, K.; Day, R. J.; Hercules, D. M. Characterization of *o*-Phenanthroline and 2,2'-Bipyridine Complexes by Laser Mass Spectrometry. *Inorg. Chem.* **1985**, *24*, 4477–4483.
(20) Pierce, J. L.; Wigley, D. E.; Walton, R. A. Homoleptic Isocyanide and Mixed Nitrosyl–Isocyanide Complexes of Chromium and Molybdenum: Secondary Ion Mass Spectrometry Studies. *Organometallics* **1982**, *1*, 1328–1331.

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Experimental Section

Fast atom bombardment (FAB) mass spectra of Ru(II) complexes were acquired with a hybrid, tandem mass spectrometer with EBQQ geometry,[28] capable of obtaining both conventional mass spectra and low-energy collision spectra. A modified FAB ion source, capable of acquiring high-pressure fast atom bombardment (HPFAB) mass spectra,[29,30] was used in a conventional manner (no addition of bath/reactant gas or ionizing filament) for these studies. There is no appreciable difference between mass spectra obtained by using the modified HPFAB ion source under the given conditions and those obtained by using a conventional FAB ion source. The ion source block and probe were operated without additional heating at a nominal temperature of 300–350 K, as measured by a thermocouple gauge. The Ru(II) complexes were dissolved in a liquid matrix of neat 3-nitrobenzyl alcohol and placed on a stainless-steel FAB probe tip. The sample was sputtered by an energetic (8 keV) beam of xenon atoms. The sputtered ions were mass analyzed in a conventional manner using the first, double-focusing mass spectrometer (EB) at a resolving power of 1000–1500. The data system was calibrated by using CsI. Mass spectra for each sample were acquired for 10–30 scans at 5–10 s/decade. The results reported here are based on the average of 1–3 scans without background subtraction of matrix ions.

The low-energy collision spectra were obtained by mass-selecting various ions with the first mass spectrometer (EB) at a resolving power of about 1000. The mass-selected Ru(II) complex ions were then transmitted into the RF-only quadrupole collision cell (Q_1) where they underwent collisions with argon as a target gas. The collision-gas pressure was adjusted to reduce the primary ion intensities to about 50% of the original intensities; this corresponds to multiple collision conditions. The collision energy (laboratory coordinates, E_{lab}) of the ions ranged from 10 to 50 eV, as indicated by measuring the potential differences between the ion source and collision cell. The fragment ions thus produced in the collision cell (Q_1) were detected by using the quadrupole mass filter (Q_2). Inefficient transmission of precursor ions occurs at higher collision energies (>20 eV), resulting in the loss of precursor ion intensity in the collision spectra. This artifact of hybrid instruments is known to us from studies of individual bond dissociation energies in a metal carbonyl.[31] The collision spectra reported here are the average of 10–15 scans at a rate of about 5–8 s per scan over the mass range shown in each figure.

The ruthenium complexes studied here were a gift, and their syntheses have in part been described previously.[9] They were used without further purification. Various analyses, including mass spectrometric identification (this study), have been used to confirm the identities of the compounds.[32] The collision gases and solvents were obtained commercially. The 3-nitrobenzyl alcohol was purified by distillation before use.

Results and Discussion

[Ru(bpy)₂(tpy)](PF₆)₂ and [Ru(bdmt)(bpy)₂](PF₆)₂. Ruthe-

Figure 1. (a) FAB mass spectrum of [Ru(tpy)(bpy)₂](PF₆)₂ (**1**). (b) FAB mass spectrum of [Ru(bdmt)(bpy)₂](PF₆)₂ (**2**).

nium(II) complexes containing π-acids such as polypyridyls are generally hexacoordinate, bonding in an octahedral fashion.[33] The [Ru(tpy)(bpy)₂](PF₆)₂ (tpy = 2,2′:6,2″-terpyridine; bpy = 2,2′-bipyridine) complex **1** and its bis(annelated derivative [Ru-

1   **2**
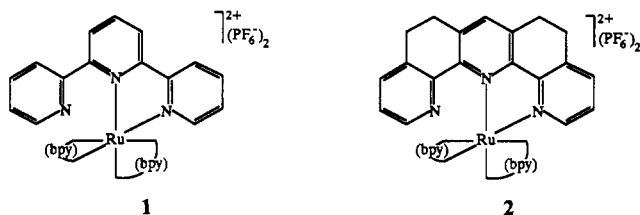
(bdmt)(bpy)₂](PF₆)₂ (bdmt = 3,3′:5,3″-bis(dimethylene)-2,2′:6,2″-terpyridine) contain two bipyridine ligands that can act in bidentate fashion. They also contain a terpyridine or terpyridine derivative that can act in a tridentate fashion, forming five-membered chelate rings that share a common bond between the center nitrogen and the metal.[9] The Ru(II) complex **2** belongs to a class of compounds that have been synthesized with annelated derivatives of 2,2′:6,2″-terpyridine.[9] In these complexes, the dihedral angles and "bite" angle of the five-member chelate ring can be controlled by the length of the bridging methylene groups. Annelated derivatives of 2,2′:6,2″-terpyridine biscoordinate with Ru^{II}(bpy)₂ in an octahedral fashion, with the ligand distorting to accommodate this geometry.[9] Thus, one of the nitrogens in the polypyridyl complexes **1** and **2** is left unchelated. Proton NMR studies of analogues of **1** and **2** containing perdeuterated (²H)-2,2′-bipyridine (dbpy) ligands have confirmed that the terpyridine and its derivative are bidentate and coordinate in an assymmetric fashion.[32]

(21) Pierce, J. L.; Busch, K. L.; Cooks, R. G.; Walton, R. A. Secondary-Ion Mass Spectra of Nonvolatile Silver Complexes. *Inorg. Chem.* **1983**, *22*, 2492–2494.

(22) Freas, R. B.; Campana, J. E. Fast-Atom Bombardment Mass Spectrometry of Phthalocyanines. *Inorg. Chem.* **1984**, *23*, 4654–4658.

(23) Bojesen, G. Fast-Atom-Bombardment Mass Spectrometry of Coordination Compounds. *Org. Mass Spectrom.* **1985**, *20*, 413–415.

(24) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. Observation of Doubly Charged Ions in Fast Atom Bombardment Mass Spectrometry: Ruthenium(II) Complexes in a Nitrobenzyl Alcohol Matrix. *Inorg. Chem.* **1987**, *26*, 560–562.

(25) Kurlansik, L.; Williams, T. J.; Campana, J. E.; Green, B. N.; Anderson, L. W.; Strong, J. M. Fast-Atom Bombardment: Evidence of Disproportionation and Recombination of a Synthetic Porphyrin in the Matrix. *Biochem. Biophys. Res. Commun.* **1983**, *111*, 478–483.

(26) *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum: New York, 1978.

(27) *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; John Wiley and Sons: New York, 1983.

(28) The mass spectrometer was a VG 70-SEQ instrument (VG Analytical Ltd., Wythenshawe, Manchester, U.K.) with EBQQ geometry (E = electrostatic sector (energy analyzer); B = magnetic sector (momentum analyzer); Q_1 = RF-only quadrupole ion guide/collision cell; Q_2 = quadrupole mass analyzer).

(29) Freas, R. B.; Ross, M. M.; Campana, J. E. Chemical Ionization/Fast-Atom Bombardment Mass Spectrometry: Ion/Molecule Reactions. *J. Am. Chem. Soc.* **1985**, *107*, 6195–6201.

(30) Thompson, T. J.; Freas, R. B. Development of Continuous-Flow High-Pressure Fast-Atom Bombardment Mass Spectrometry: Studies of Polyethylene Glycols. Manuscript in preparation.

(31) Yu, W.; Liang, X.; Freas, R. B. Unimolecular Dissociation Kinetics and Collision-Induced Dissociation of [Mn₂(CO)₁₀)]⁺: Determination of Individual Bond Dissociation Energies *J. Phys. Chem.*, submitted for publication.

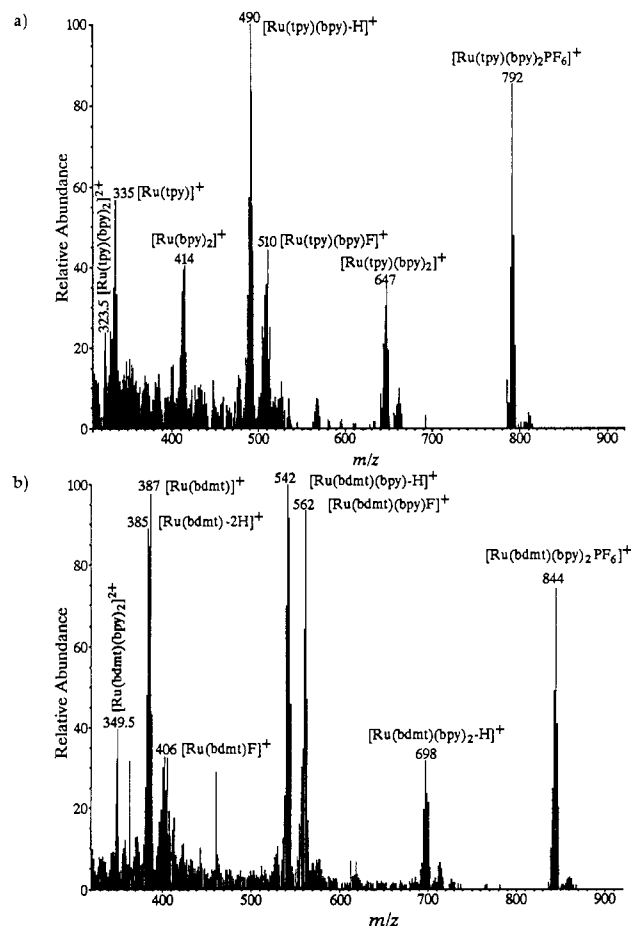(32) Thummel, R. P., University of Houston, personal communication, 1989.

(33) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 3rd Ed.; Wiley & Sons: New York, 1972; p 1001.

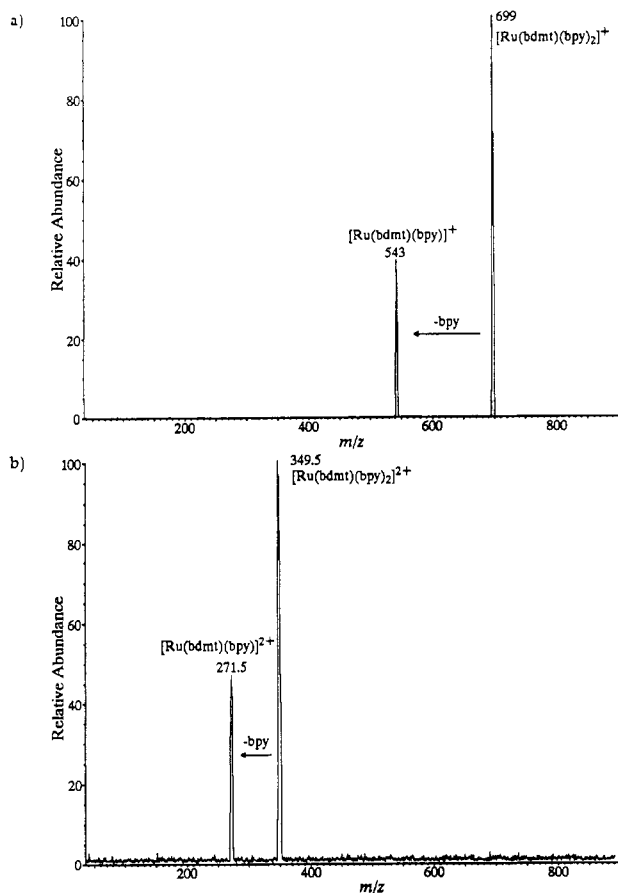**Figure 2.** (a) Low-energy collision spectrum of [Ru(bdmt)(bpy)$_2$]$^+$ (m/z 699). (b) Low-energy collision spectrum of [Ru(bdmt)(bpy)$_2$]$^{2+}$ (m/z 349.5).

Figure 1 shows the fast atom bombardment mass spectra of **1** and **2**. The FAB mass spectra of these complexes are for the most part representative of the FAB mass spectra of several (polypyridyl)ruthenium(II) complexes that we have studied. The use of 3-nitrobenzyl alcohol as a liquid matrix provides abundant ions from the analyte with a good signal-to-noise ratio, although other matrices have been used successfully for similar and other organometallic compounds.[17,24,34-36]

A number of informative fragment ions are observed in the FAB mass spectra in Figure 1. The highest mass ions [Ru(bdmt)-(bpy)$_2$PF$_6$]$^+$ at m/z 844[37] and [Ru(tpy)(bpy)$_2$PF$_6$]$^+$ at m/z 792 correspond to the loss of a PF$_6^-$ counterion. In these ions, ruthenium maintains a formal oxidation state of +2. The loss of a single counterion to form the singly charged Ru(II) ion is consistently the highest mass ion and among the most abundant ions that were observed for the various derivatives studied. The doubly charged ions [Ru(bdmt)(bpy)$_2$]$^{2+}$ at m/z 349.5 and [Ru(tpy)(bpy)$_2$]$^{2+}$ at m/z 323.5 were identified by ions occurring with half mass separation at the expected abundances in the isotopic cluster. The formation of doubly charged ions from a 3-nitrobenzyl alcohol matrix is similar to what has been previously been reported for (polypyridyl)ruthenium(II) complexes.[24]
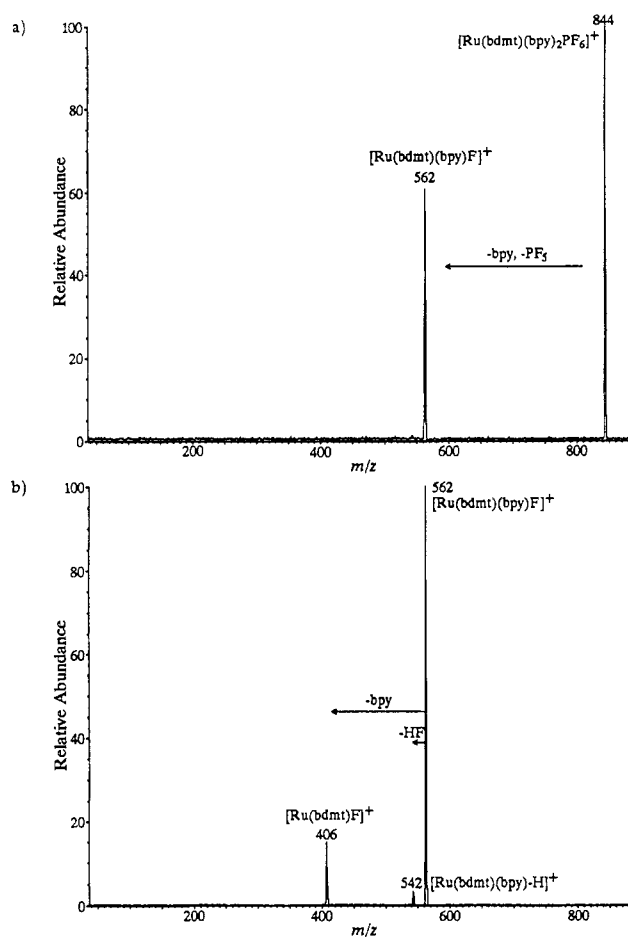

Figure 3. (a) Low-energy collision spectrum of [Ru(bdmt)(bpy)$_2$(PF$_6$)]$^+$ (m/z 844). (b) Low-energy collision spectrum of [Ru(bdmt)(bpy)F]$^+$ (m/z 562).

The low-energy CID spectra of [Ru(bdmt)(bpy)$_2$]$^+$ at m/z 699 and [Ru(bdmt)(bpy)$_2$]$^{2+}$ at m/z 349.5 are compared in Figure 2. Both the singly charged and doubly charged ions exhibit only the loss of one bipyridine ligand under low-energy (E_{CM} = 1–2 eV) collision conditions. The low-energy collision spectra of doubly charged ions from other [Ru(L)(bpy)$_2$]$^+$ complexes are also unexceptional and exhibit the loss of a bipyridine ligand. In the terpyridine derivatives, NMR studies have identified the normally tridentate terpyridine ligands as being only bidentate.[32] Examination of the collision spectra of doubly charged ions indicates that during collisional activation (or during ionization) the complex rearranges so that the terpyridine becomes more tightly bound, perhaps by increasing its denticity to three. The loss of a bidentate bis(dimethylene)terpyridine would be expected to be competitive with the loss of (bidentate) bipyridine ligands, as either of these two processes would require the cleavage of two Ru–N chelate bonds. On the other hand, the loss of a tridentate terpyridine ligand would require the cleavage of three Ru–N bonds and therefore would not be competitive with the more facile elimination of a bidentate ligand with two Ru–N bonds.

An abundant ion having the formula [Ru(bdmt)(bpy)F]$^+$ is observed at m/z 562. The question arises as to the formation of this ion. One possibility is that the ion arises from radiation-induced damage of the analyte within the matrix and direct recombination[38] to form a complex with an F$^-$ counterion. Another possibility is that the fluoride-containing fragment ion is due to a gas-phase rearrangement or unimolecular dissociation with concomitant loss of neutral PF$_5$ and retention of F$^-$ as a ligand in the complex. Fluoride extractions have been observed from

(34) Miller, J. M. Fast-Atom Bombardment Mass Spectrometry and Related Techniques. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeléus, H. J., Sharpe, A., Eds.; Academic: Orlando, FL, 1984; Vol. 28, pp 1–27.

(35) Miller, J. M. Fast-Atom Bombardment (FAB) Mass Spectrometry: A New Technique for the Organometallic Chemist. *J. Organomet. Chem.* **1983**, *249*, 299–302.

(36) Miller, J. M. Fast-Atom Bombardment Mass Spectrometry (FAB MS) of Organometallic, Coordination, and Related Compounds. *Mass Spectrom. Rev.* **1989**, *9*, 319–347.

(37) Ruthenium has several isotopes, the most abundant having a mass of 102 u. For the purpose of clarity, the nominal mass (i.e. for ^{102}Ru) will be used when referring to the isotopic cluster of a particular ion.

(38) Murray, P. T.; Rabalais, J. W. Ejection Dynamics and Electronic Processes Governing Secondary Particle Emission in SIMS. *J. Am. Chem. Soc.* **1981**, *103*, 1007–1013.

SF_6 bath gas in the HPFAB technique.[39] Thus, the low-energy collision-induced dissociation of $[Ru(bdmt)(bpy)_2PF_6]^+$ (*m/z* 844) was examined to probe the possibility of gas-phase rearrangements. The collision spectrum is shown in Figure 3. The concerted loss of a bipyridine ligand and a neutral PF_5 was observed at low collision energies to yield a $[Ru(bdmt)(bpy)F]^+$ fragment ion at *m/z* 562. In the metastable or unimolecular dissociation spectra, the only fragment ion that was observed corresponded to the loss of the counterion PF_6^- from $[Ru(bdmt)(bpy)_2PF_6]^+$. The loss of a bipyridine ligand opens one or two coordination sites in a hexacoordinate Ru(II) complex. The bis(dimethylene)terpyridine ligand can now become tridentate, and the remaining bipyridine can be bidentate resulting in a pentacoordinate complex. A fluoride transfer from PF_6^- can now occur to form a hexacoordinate Ru(II) complex. The formation of this hexacoordinate ion via a ligand transfer from the outer-sphere coordination shell to an inner-sphere coordination site may be facilitated by Coulombic attraction between $[Ru(bdmt)(bpy)]^{2+}$ and F^-. The fact that the fluoride ion is an inner-sphere ligand is suggested by the absence of any $[Ru(bdmt)(bpy)_2F]^+$ in either the collision of FAB mass spectrum. In a $[Ru(bdmt)(bpy)_2F]^+$ ion (which was not observed), there would be seven nitrogens available for chelation filling all six coordination sites and the fluoride counterion would be retained by the same Coulombic attraction that retains the PF_6^- counterion. Consequently, the above observations suggest that the fluoride counter does not arise from radiation-induced damage of the matrix. Further, the fluoride-containing ions can arise from facile gas-phase dissociations in the FAB ion source, as suggested by collision spectra.

Figure 3 also shows the low-energy CID spectrum of $[Ru(bdmt)(bpy)F]^+$ (*m/z* 562). The two fragmentations that were observed correspond to the loss of HF (*m/z* 542) and the loss of a bipyridine ligand (*m/z* 406). An ion at *m/z* 542 was also observed in the CID spectrum of $[Ru(bdmt)(bpy)_2PF_6]^+$ (*m/z* 844) at higher collision energies. The loss of HF occurs when a ligand with a freely rotating pyridyl group such as bipyridine is attached to the Ru metal center in the annelated derivative. The fluoride ion is retained when the loss of bipyridine from *m/z* 562 occurs. This observation corroborates the intramolecular oxidative-addition mechanism proposed by Cerny et al. to explain the formation of deprotonated $[Ru(bpy)x-H]^+$ (*x* = 1, 2).[17] Rotation around the 2,2'-(C–C) bond of the bipyridine ligand occurs with oxidative addition via metal insertion into the 3-(C–H) bond. Reductive elimination of HF and formation of a carbon-bound Ru(II) metal center can then occur. In addition, we have not observed any evidence for oxidative addition or C–H bond activation in the collision spectra of the bisannelated terpyridine. This suggests that the above mechanism is substantially correct, as free rotation to form a carbon-bound ruthenium cannot occur in the bisannelated terpyridines. The oxidative addition of group 8 atomic metal ions to C–H and C–C bonds in the gas phase is well-known.[40] In particular, the second-row group 8 atomic ions (Ru(I), Rh(I), Pd(I)) have been reported to dehydrogenate alkanes in the gas phase by a 1,2-elimination.[41] Thus, the coordinatively or nearly coordinatively saturated (polypyridyl)ruthenium(II) complexes exhibit chemistry similar to that of the coordinatively unsaturated atomic ion Ru^+.

The collision spectra of $[Ru(tpy)(bpy)_2PF_6]^+$ and $[Ru(tpy)(bpy)F]^+$ are compared in Figure 4 in an attempt to probe their reactions further. The collision spectra of the counterion-containing complex again shows the abundant, concerted losses of a polypyridyl ligand (bpy, tpy) and a neutral PF_5. The loss of HF to form the deprotonated species was also observed. Figure
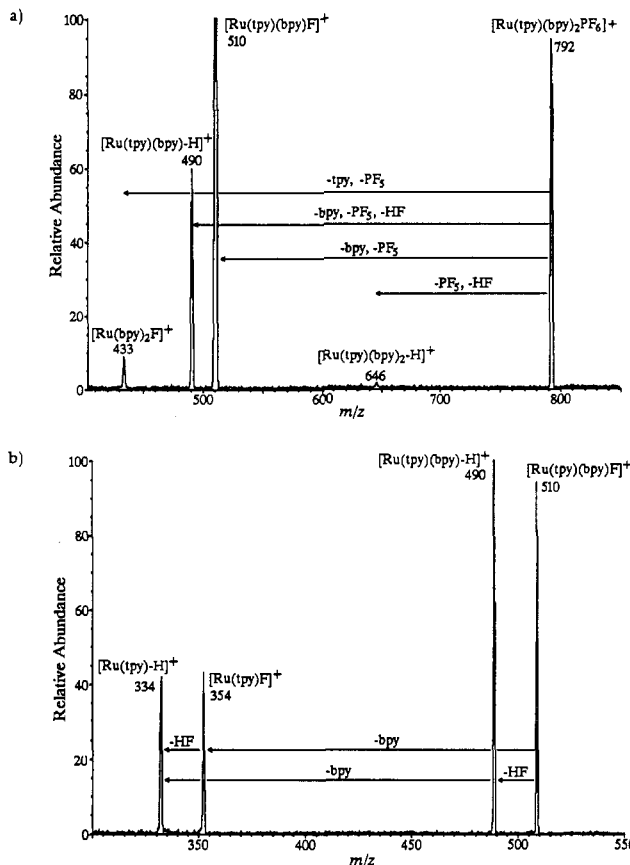

Figure 4. (a) Low-energy collision spectrum of $[Ru(tpy)(bpy)_2PF_6]^+$ (*m/z* 792). (b) Low-energy collision spectrum of $[Ru(tpy)(bpy)F]^+$ (*m/z* 510).

4 shows the CID spectrum of $[Ru(tpy)(bpy)F]^+$ at a collision energy of nearly 6 eV (E_{CM}). The $[Ru(tpy)F]^+$ and $[Ru(tpy) - H]^+$ fragments disappear when the collision energy is less than 5.1 eV (E_{CM}). This indicates that the loss of a bipyridine requires more energy than the elimination of HF. In addition, the loss of the terpyridine ligand was not observed even at the higher collision energy. In this ion, the terpyridine would be expected to be tridentate, with the fluoride ion occupying the remaining site in a hexacoordinate Ru(II) complex. For the ion to eliminate HF via the above-mentioned intramolecular oxidative addition, the mechanism could proceed via a heptacoordinate Ru(III) intermediate or via a concerted loss of HF from a hexacoordinate ruthenium.

The ruthenium metal center appears to prefer to retain its formal oxidation state of +2. The abundant ions $[Ru(bdmt)(bpy)_2 - H]^+$ (*m/z* 698) and $[Ru(bdmt)(bpy) - H]^+$ (*m/z* 542) correspond to losses of the counterions and a hydrogen. The formal loss of a proton maintains an oxidation state of Ru(II) in the singly charged ions. The deprotonated $[Ru(bpy)x-H]^+$ (*x* = 1, 2) ions have been reported to be a common feature in the mass spectra of the corresponding Ru(II) complexes.[17] The mechanism that has been postulated for the formation of these ions assumes that coordinatively unsaturated Ru(II) complexes undergo an intramolecular oxidative addition. This mechanism appears to be confirmed by the fact that $[Ru(bdmt) - H]^+$ was not observed. In **2**, the bis(dimethylene) ring annelation prevents free rotation around the C–C bonds. However, the loss of two hydrogen atoms during FAB ionization to form $[Ru(bdmt) - 2H]^+$ (*m/z* 385) was observed. This latter ion could correspond to the elimination of H_2, possibly via a 1,2-elimination from a bridging dimethylene group. The loss of two H's is discussed later with respect to the fragmentation in the FAB mass spectrum of $[Ru_n(oddp)-(bpy)_{2n}](PF_6)_{2n}$.

Examination of the isotope clusters at *m/z* 647, 490, 414, and 335 in the FAB mass spectrum of **1** and *m/z* 698 and 542 in the FAB mass spectrum of **2** reveals the presence of the corresponding

(39) Callahan, J. H.; Colton, R. J.; Ross, M. M. High pressure fast-atom bombardment mass spectrometry: collisional stabilization and reactions of alkali halide cluster ions. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *90*, 9–38.

(40) Allison, J. Freas, R. B.; Ridge, D. P. Cleavage of Alkanes by Transition Metal Ions in the Gas Phase. *J. Am. Chem. Soc.* **1979**, *101*, 1332–1333.

(41) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. Activation of Alkanes by Ruthenium, Rhodium, and Palladium ions in the Gas Phase: Striking Differences in Reactivity of First- and Second-Row Metal Ions. *J. Am. Chem. Soc.* **1986**, *108*, 5675–5683.
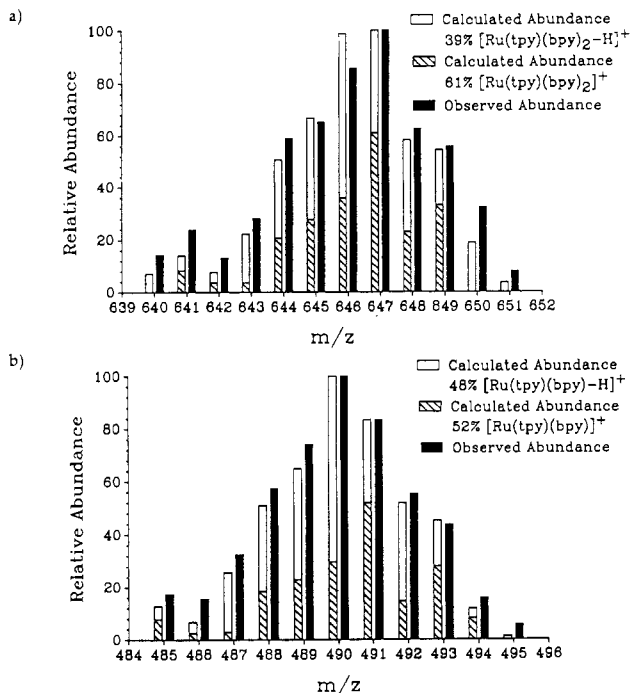
a)

b)

Figure 5. (a) Comparison of isotope abundances for a theoretically calculated cluster containing 39% [Ru(tpy)(bpy) – H]$^+$ (blank bar) and 61% [Ru(tpy)(bpy)]$^+$ (scribed bar) and experimentally observed isotope abundances (solid bar). (b) Comparison of isotope abundances for a theoretically calculated cluster containing 48% [Ru(tpy)(bpy) – H]$^+$ (blank bar) and 52% [Ru(tpy)(bpy)]$^+$ (scribed bar) and experimentally observed isotope abundances (solid bar).

deprotonated [Ru(L)$_x$(bpy)$_y$ – H]$^+$ (x = 0, 1; y = 0–2; L = tpy, bdmt) complexes and [Ru(L)$_x$(bpy)$_y$]$^+$ (x = 0, 1; y = 0–2; L = tpy, bdmt) complexes that contain ruthenium in a formal oxidation state of +1. Figure 5 shows a comparison of isotope abundances for theoretically calculated clusters containing [Ru(tpy)(bpy)$_x$ – H]$^+$ and [Ru(tpy)(bpy)$_x$]$^+$ (x = 1, 2) and experimentally observed isotope abundances. The abundances of the deprotonated Ru(II) and the Ru(I) species were deconvoluted by finding the best fit (by minimizing the average absolute deviation) to the sum of the abundances for the ten major isotope components in each cluster. The abundance of the deprotonated species was found to have values of 39%, 48%, 34%, and 33% relative to the base peak in the isotope clusters at m/z 647, 490, 414, and 335. The deprotonated ion can be due to the intramolecular oxidative-addition mechanism described above and observed for analogous Ru(II) complexes.[17,24] On the other hand, ruthenium(II) has an electron-deficient configuration capable of capturing an electron. Abundant secondary electrons are produced in the particle-induced desorption process. The formation of the singly charged ion [Ru(bdmt)(bpy)$_2$]$^+$ could arise from electron capture (reduction) during the sputtering process.

Careful examination of the FAB mass spectrum of 1 in Figure 1 reveals an ion at m/z 569 corresponding to the loss of 78 (C$_5$H$_4$N) from m/z 647. The loss of a pyridyl group would arise from a simple C–C bond cleavage in either the terpyridine or bipyridine ligand. This loss would suggest that the ruthenium complex is in fact hexacoordinate with one of the polypyridyl ligands containing a pendant pyridyl group with an unchelated nitrogen. For comparison, the collision spectrum of the ion at m/z 647 ([^{103}Ru(tpy)(bpy)$_2$ – H]$^+$/[^{102}Ru(tpy)(bpy)$_2$]$^+$) shown in Figure 6 exhibits abundant loss of a pyridyl group as well as the loss of a ligand (tpy, bpy). Again, the loss of a bipyridine ligand was observed to be more facile than the loss of a terpyridine ligand. This once again suggests that, during FAB ionization or during collisional activation, a terpyridine ligand becomes more tightly bound to the ruthenium metal center than does a bipyridine ligand. This observation is again suggestive of a tridentate terpyridine, as ligand loss via the cleavage of two chelating Ru–N bonds would be expected to be competitive.
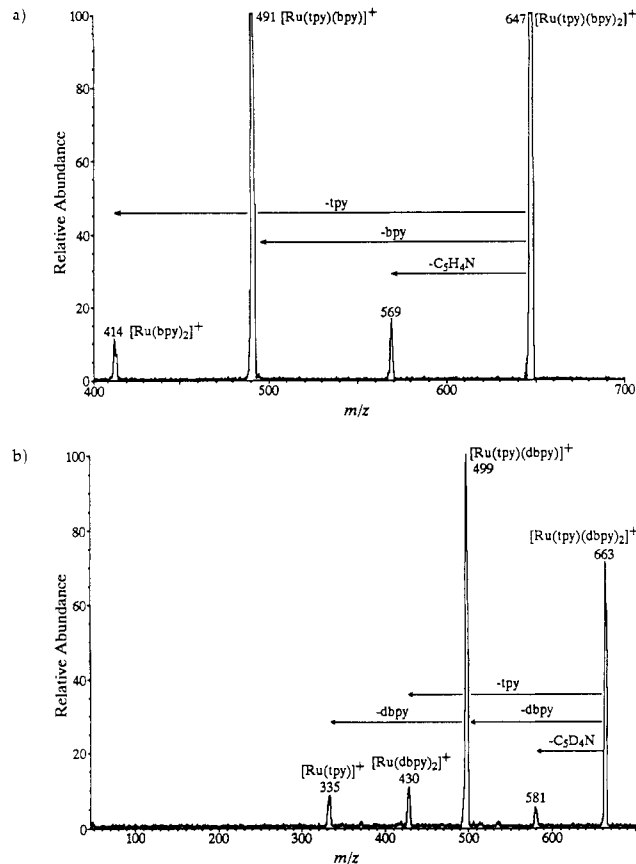
a)

b)

Figure 6. (a) Low-energy collision spectrum of [^{102}Ru(tpy)(bpy) – H]$^+$/[^{101}Ru(tpy)(bpy)$_2$]$^+$ (m/z 647). (b) Low-energy collision spectrum of [Ru(tpy)(dbpy)$_2$]$^+$ (m/z 663).

The question arises as to whether the loss of the pyridyl group comes from the terpyridine, which is assymetrically bidentate in the condensed phase and has a pendant pyridyl group, or whether the loss of a pyridyl group arises from a bipyridine ligand or both. The results discussed above suggest that upon activation or during ionization, the terpyridine becomes tridentate. If in fact the ruthenium remains hexacoordinate, one of the bipyridines must contain a pendant pyridyl group with an unchelated nitrogen. The question can now be addressed by examining the collision spectra of various ions in the FAB mass spectrum of the [Ru(tpy)-(dpy)$_2$](PF$_6$)$_2$ (dbpy = (^{2}H)2,2′-bipyridine), where both of the bipyridine ligands are fully deuterated. Examination of the collision spectrum of [Ru(tpy)(dbpy)$_2$]$^+$ in Figure 6 shows exclusive loss of C$_5$D$_4$N. In fact the collision spectrum of [Ru-(tpy)(dbpy)$_2$]$^+$ shows quite clearly that the loss of a terpyridine ligand is competitive with the elimination of a pair of bidentate ligands. Consequently, this observation corroborates the postulate that upon activation by collision or ionization the terpyridine becomes tridentate on a hexacoordinate ruthenium metal center.

[(Ru(bpy)$_2$)$_x$(oddp)](PF$_6$)$_{2x}$ (x = 1, 2). The phenanthroline derivative 5,6,9,10,11,12,15,16-octahydrocycloocta[1″,2″:5,6;-4″,3″:5′,6′]dipyrido[2,3-b:2′,3′-b]di[1,10]phenanthroline (oddp) can accommodate two Ru(bpy)$_2$ groups because the tetramethylene bridging group twists the halves of the ligand out of plane.[8] Some of the abundant ions in the FAB mass spectrum of the (Ru(bpy)$_2$)$_1$ (3) and (Ru(bpy)$_2$)$_2$ (4) complexes are listed

3

4
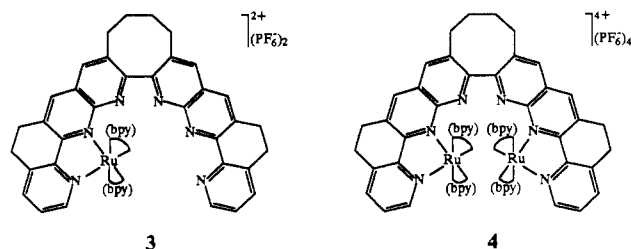
Table I. Abundant Ions in the FAB Mass Spectra of
[Ru$_x$(oddp)(bpy)$_{2x}$] (x = 1, 2)

m/z	stoichiometry	rel abund[a]
	x = 1	
1077	[Ru(oddp)(bpy)$_2$PF$_6$]$^+$	77
933	[Ru(oddp)(bpy)$_2$]$^+$	100
795	[Ru(oddp)(bpy)F]$^+$	27
775	[Ru(oddp)(bpy) – H]$^+$	75
620	[Ru(oddp)]$^+$	91
466.5	[Ru(oddp)(bpy)$_2$]$^{2+}$	81
	x = 2	
1781	[Ru$_2$(oddp)(bpy)$_4$(PF$_6$)$_3$]$^+$	100
1636	[Ru$_2$(oddp)(bpy)$_4$(PF$_6$)$_2$]$^+$	94
1491	[Ru$_2$(oddp)(bpy)$_4$(PF$_6$)]$^+$	31
1346	[Ru$_2$(oddp)(bpy)$_4$]$^+$	13
1187	[Ru$_2$(oddp)(bpy)$_3$ – 3H]$^+$	41
1031	[Ru$_2$(oddp)(bpy)$_2$ – 3H]$^+$	62
875	[Ru$_2$(oddp)(bpy) – 3H]$^+$	57
719	[Ru$_2$(oddp) – 3H]$^+$	55

[a]Abundances are relative to 100 for the most abundant analyte ion listed.

in Table I. In general, the ions that were observed in the FAB mass spectrum of the monoruthenium complex **3** correspond to the same fragmentation processes that have been described before. The abundance of the doubly charged ion [Ru(bpy)$_2$(oddp)]$^{2+}$ was almost the same as the corresponding singly charged ion. This suggests that the process for the formation of the doubly charged ion is more facile for the complexes containing the larger cavity-shaped molecule. The formation of the doubly charged ion is thought to proceed via an oxidative quenching process of an excited state by nitroaromatic compounds such as 3-nitrobenzyl alcohol.[24] The quenching of an excited-state complex [RuL$_3$]$^{2+*}$ (L is a 2,2'-bipyridine or 1,10-phenanthroline derivative) by various oxidants is known.[42] In [(Ru(bpy)$_2$)$_x$(oddp)](PF$_6$)$_{2x}$, the more extended conjugation system of the cavity-shaped ligand provides for more delocalization and lower lying excited states perhaps facilitating the quenching process.

The abundances of fragment ions of the bis(ruthenium) complex are listed also in Table I. For the most part the high-mass fragment ions correspond to the simple loss of PF$_6$ counterions except, in this case, there are four counterions. In addition to these ions, isotope clusters at m/z 1187, 1031, 875, and 719 were observed that correspond to the loss of all counterions, the loss of one to four bipyridines, and the loss of three protons. The loss of three protons maintains each ruthenium in a formal oxidation state of +2 for a singly charged ion. However, observation of the ions at m/z 719 and 875 suggests that a different mechanism for deprotonation is required. This is in contrast to the above studies of the terpyridine derivatives, where the deprotonation was thought to occur by reductive elimination following formation of a metallacarbacycle via oxidative addition to the 3-C–H bond. In the case of the phenanthroline derivatives [(Ru(bpy)$_2$)$_x$(oddp)](PF$_6$)$_{2x}$, the large cavity-shaped ligand may be effectively shielding the PF$_6^-$ counterion from the ruthenium and therefore the loss of the counterion occurs concurrent with extraction of a proton, possibly from one of the bridging methylene units. This type of mechanism is also corroborated by the observation of the loss of two protons from the bisannelated terpyridine derivative **2** to form an ion at m/z 385. Multiple proton losses were observed to be abundant only in ring systems containing polymethylene bridges. Unfortunately, the abundances of the high-mass ions in the FAB mass spectrum of the bis(ruthenium) complex **4** were insufficient to obtain CID spectra to confirm these or other mechanisms.

The low-energy collision spectra of the ions m/z 1077 [Ru-(oddp)(bpy)$_2$PF$_6$]$^+$ and m/z 932 [Ru(oddp)(bpy)$_2$]$^+$ in the FAB mass spectrum of the mono(ruthenium) complex **3** are shown in

(42) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. Poly(pyridine)ruthenium(II)-Photoinduced Redox Reactions of Bipyridinium Cations, Poly(pyridine)rhodium Complexes, and Osmium Ammines. *J. Am. Chem. Soc.* **1982**, *104*, 3618–3627.
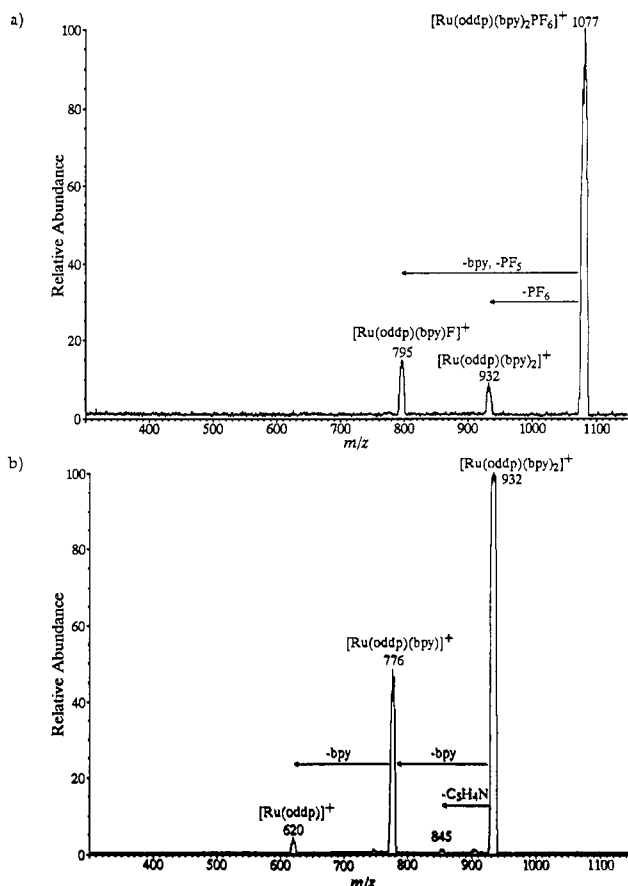

Figure 7. (a) Low-energy collision spectrum of [Ru(oddp)(bpy)$_2$(PF$_6$)]$^+$ (m/z 1077). (b) Low-energy collision spectrum of [Ru(oddp)(bpy)$_2$]$^+$ (m/z 932).

Table II. Abundant Ions in the FAB Mass Spectrum of [Ru(bdmi)(bpy)$_2$](PF$_6$)$_2$

m/z	stoichiometry	rel abund[a]
719	[Ru(bdmi)(bpy)$_2$PF$_6$]$^+$	84
593	[Ru(bdmi)(bpy)$_2$F]$^+$	82
573	[Ru(bdmi)(bpy)$_2$ – H]$^+$	58
433	[Ru(bpy)$_2$F]$^+$	88
413	[Ru(bpy)$_2$ – H]$^+$	100

[a]Abundances are relative to 100 for the most abundant analyte ion listed.

Figure 7. The low-energy collision spectrum of [Ru(oddp)-(bpy)$_2$PF$_6$]$^+$ shows two fragments: [Ru(oddp)(bpy)$_2$]$^+$ (m/z 932) and [Ru(oddp)(bpy)F]$^+$ (m/z 795). The loss of PF$_5$ and a bipyridine ligand to form m/z 795 corresponds to a fluoride transfer to the ruthenium. This is consistent with the CID of terpyridine derivatives of ruthenium. However, the abundant loss of just the counterion from [Ru(oddp)(bpy)$_2$PF$_6$]$^+$ contrasts with the collision spectra of the terpyridine derivatives. This contrast suggests that there may in fact be considerable shielding of the counterion from the ruthenium, consistent with the postulated mechanism for the multiple deprotonation from the polymethylene bridges by the counterions in the phenanthroline derivatives [(Ru(bpy)$_2$)$_x$-(oddp)](PF$_6$)$_{2x}$.

The collision-induced fragmentations of [Ru(oddp)(bpy)$_2$]$^+$ (Figure 7) consist of the loss of intact ligands and several other less abundant ions. The loss of a pyridyl group at m/z 854 can only come from one of the bipyridines. On the other hand, the loss of 15 and 28 from the precursor and the major fragment ion at m/z 776 suggests that the bridging methylene groups are being activated. This observation is again consistent with the postulated mechanism for multiple deprotonation, by showing that the bridging methylenes are reactive.

[Ru(dmbi)(bpy)$_2$H$_2$O](PF$_6$)$_2$ and [Ru(tpd)(tpy)](PF$_6$)$_2$. The FAB mass spectrum of two additional compounds have been

Table III. Abundant Ions in the FAB Mass Spectrum of [Ru(tpy)(tpd)](PF$_6$)$_2$

m/z	stoichiometry	rel abund[a]
868	[Ru(tpy)(tpd)PF$_6$]$^+$	24
742	[Ru(tpy)(tpd)F]$^+$	N/O
722	[Ru(tpy)(tpd) − H]$^+$	67
644	[Ru(tpy)(tpd) − C$_5$H$_5$N]$^+$	10
509	[Ru(tpd)F]$^+$	8
489	[Ru(tpd) − H]$^+$	17
411	[Ru(tpd) − C$_5$H$_5$N]$^+$	12
334	[Ru(tpy) − H]$^+$	100

[a] Abundances are relative to 100 for the most abundant analyte ion listed.

examined to determine the effect of shielding of the counterion from the ruthenium center by polypyridyl ligands and hence modification of the outer-sphere/inner-sphere fluoride-transfer process. The first of these, [Ru(bdmi)(bpy)$_2$H$_2$O](PF$_6$)$_2$ (5) (bdmi

5

6
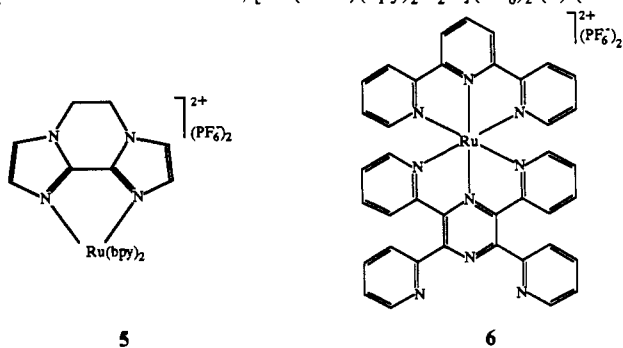
= N,N'-dimethylene-2,2'-biimidazole), contains a ligand whose bite angle is highly constrained by the bridging dimethylene. This ligand would be expected to be monodentate. A list of abundant ions in the FAB mass spectrum of 5 are given in Table II. An abundant ion is observed at m/z 593 corresponding to [Ru-(bdmi)(bpy)$_2$F]$^+$. In this ion, fluoride transfer has occurred without the loss of any chelated ligand. The low-energy collision spectrum of m/z 719 [Ru(bdmi)(bpy)$_2$PF$_6$]$^+$ shows only the fragment ion at m/z 593. In addition, the low-energy collision spectrum of m/z 593 shows only the loss of the biimidazole ligand. These observations indicate the facile transfer of F$^-$ to an open coordination site.

The abundant ions in the FAB mass spectrum of the terpyridine derivative [Ru(tpy)(tpd)](PF$_6$)$_2$ (6) (tpd = 2,3,5,6-tetra-2'-pyridyl-1,4-diazine) are listed in Table III. In contrast to the case for 5, the F$^-$ transfer was not observed to be a facile process for 6. In fact, the only ion that was identified as containing a fluoride ligand contains only one polypyridyl ligand, and it is significantly less abundant than the other fragment ions. Thus, the tridentate ligands effectively shield the ruthenium from substantial interaction with the counterion and F$^-$ transfer does not occur.

Conclusions

The highest mass ion observed for these Ru(II) ions consistently corresponded to [(Ru)$_x$(bpy)$_{2x}$(L)(PF$_6$)$_{x-1}$]$^+$. Abundant doubly charged ions can be observed in 3-nitrobenzyl alcohol matrix. Low-energy collision-induced dissociation of the doubly charged ions was observed to yield the simple loss of an intact ligand, and the CID fragmentation pathway was charge independent. The predominant fragment ions in the CID spectra are due to losses of intact ligands and a neutral PF$_5$. A fluoride transfer from the PF$_6^-$ counterion to the metal center was observed when the ions from the ruthenium complex became less than hexacoordinate due to ligand losses or inability to fill the coordination sphere. Further fragmentation can be explained by assuming an intra-molecular oxidative addition of the metal to the polypyridine to form a carbon-bound metallacarbacycle.

In the CID spectra of the terpyridine derivatives, all of the fragment ions of the Ru(II) precursors retain what can formally be assigned as a Ru(II) center. We have not noted the loss of fragments under low-energy collision conditions that give rise to a formal Ru(I) oxidation state. This observation suggests that the formation of the Ru(I) species primarily occurs during desorption from the matrix by secondary electron capture or by a matrix-assisted one-electron reduction.

Thus, fast atom bombardment tandem mass spectrometry is useful for the determination of the fragmentation pathways of polypyridyl complex ions. In addition, descriptive chemistry of complexes and their fragment ions can be obtained that in many cases parallels that of condensed-phase processes. Such processes can be used to identify additional reaction channels of a novel and important class of organometallic complexes.