Fast Atom Bombardment Mass Spectrometry of Multiply Charged Polynuclear Rhenium(I)-Ruthenium(II) Complexes

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The fast atom bombardment (FAB) mass spectrometric behavior of some involatile polynuclear rhenium(I)-ruthenium(II) complexes of general formula $[Re(CO)_3(phen)(CN)-[Ru(bpy)_2(CN)]n-Ru(bpy)_2(CN)]^{(n+1)+}$ (n = 0-2, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) is presented. Singly, doubly, and, for n = 2, also triply charged ions were detected, and the fragmentation patterns of these ionic species were determined by studying unimolecular dissociation reactions. The decomposition pathways involve losses of CO and bpy neutral ligands, oxidative addition of coordinated bpy with expulsion of HX (X = CN^-, PF_6^-), and cleavage of the CN-Ru bond.

Introduction

In recent years different mass spectrometric techniques have been successfully developed for the characterization of low volatility transition metal complexes such as field desorption (FD),[1] secondary-ion mass spectrometry (SIMS),[2] laser desorption (LDMS)[3] and plasma desorption mass spectrometry (PDMS),[4] thermospray (TSP),[5] electrohydrodynamic (EHMS)[6] and fast atom bombardment mass spectrometry (FAB).[7,8]

Singly charged ions are usually produced with these techniques; however doubly charged ions have also been observed. $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ are formed[6] using electrohydrodynamic mass spectrometry and several $[RuL_3]^{2+}$ ionic species have been detected in FAB spectra.[7-11] Noteworthy in the mass spectrometric behavior of oligomeric (polypyridine)Ru^{II} complexes[12] is the presence of the doubly charged intact cation $[(NC)Ru(bpy)_2(CN)Ru(bpy)_2(NC)Ru(bpy)_2(CN)]^{2+}$ in fairly high abundance.

The importance of the FAB technique in the organometallic field is connected with the detection, in the spectra of most samples, of both the parent ion and decomposition fragments. This provides information on the molecular weight and on the structures of the molecules under investigation, since the FAB process is sufficiently energetic to promote various cleavage, rearrangement and recombination processes.

In the recent development of supramolecular photochemistry a relevant role has been played by the synthesis of molecular assemblies in which the occurrence and directionality of photoinduced intramolecular energy or electron transfer processes can be controlled.[13-17] In the context of these studies, a series of polynuclear Re(I)-Ru(II) complexes of general formula $[Re(CO)_3(phen)(CN)-[Ru(bpy)_2(CN)]_n-Ru(bpy)_2(CN)]^{(n+1)+}$ (n = 0-2, where bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline) have been recently prepared. The purpose was the study of the efficiency of long-range intercomponent energy transfer from the metal-to-ligand charge transfer excited state localized on the Re(phen) unit to that localized on the terminal Ru(bpy) center. A detailed account of synthetic procedures and electrochemical, spectroscopic and photophysical properties of these complexes will be given in a separate paper.[18]

We report here the FAB mass spectrometry of a series of binuclear, trinuclear and quadrinuclear complexes of this class, shown in Chart I.

Singly, doubly and, in the case of quadrinuclear complexes **11-12**, also triply charged ions were detected and the fragmentation pathways of all these ionic species have been studied by unimolecular dissociation reactions.[19] This technique allows the identification of all the daughter ions generated from a selected parent ion. Since the decomposition pathways of a singly or multiply charged parent ion is dependent on the ion structure, the study of unimolecular decomposition reactions represents a useful tool in ion characterization.[19]

The preferential channels of decomposition for the triply charged ions as well as for the singly and doubly charged ions of the quadrinuclear species are simple bond cleavages and ligand losses, suggesting the minor role played by the charge on the gas-phase fragmentation of these ions.

Experimental Section

Fast atom bombardment mass spectra were recorded on a double-focusing, reversed geometry ZAB 2F instrument (VG Analytical,

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Chart I

$Ru(bpy)_2(CN)_2$	1
$Ru(phen)_2(CN)_2$	2
$Re(CO)_3(phen)Cl$	3
$Re(CO)_3(phen)(CN)$	4
$[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)]PF_6$	5
$[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)]PF_6$	6
$[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)]PF_6$	7
$[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$	8
$[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$	9
$[(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$	10
$[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_3$	11
$[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_3$	12

Manchester, UK),[20] operating with a resolving power of 10000 (10% valley definition). The bombarding xenon atom beam was formed from xenon ions possessing a translational energy of 8 keV. Metastable transitions were detected in the second field free region of the instrument by means of MIKE spectra.[19] The metal complexes were dissolved in a matrix of neat 3-nitrobenzyl alcohol and placed on a stainless steel FAB probe tip. The use of 3-nitrobenzyl alcohol as liquid matrix provides abundant ions from the analyte with a good signal-to-noise ratio.

All the metastable transitions discussed in this paper for singly, doubly or triply charged species refer to the loss, from the selected parent ion, of neutral fragments.

Results and Discussion

Abbreviations and structures not implying stereochemical information but providing a pictorial representation have been used in the schemes and figures describing the fragmentation patterns.

All the m/z values given in the paper refer to ^{187}Re and ^{102}Ru isotopes.

Mononuclear Re(I) and Ru(II) Complexes. The fast atom bombardment mass spectra of $Ru(bpy)_2(CN)_2$ (**1**) and $Ru(phen)_2(CN)_2$ (**2**) have already been described in a previous paper.[12] The relevant chemistry of these Ru(II) complexes, detected as protonated molecular ions, consists of losses of neutral bpy or phen ligands, of HCN or 2HCN, of bpy + HCN and phen + HCN. Also the Re(I) complexes $Re(CO)_3(phen)Cl$ (**3**) and $Re(CO)_3(phen)(CN)$ (**4**) are observed as protonated molecular species, with $[\mathbf{3} + H]^+$ and $[\mathbf{4} + H]^+$ being the most abundant peaks of their respective spectra. The fragmentation pattern of $[\mathbf{3} + H]^+$ and $[\mathbf{4} + H]^+$, as obtained by metastable ion kinetic energy spectra (MIKE) of the preselected ions, is quite simple with losses of carbon monoxides(s) or CO associated with HX, as summarized in Table I.

In a previous work,[21] the FAB mass spectrometric behavior of $Re(CO)_3(bpy)Cl$ has been investigated, using glycerol as matrix. The base peak observed was $[M - Cl]^+$ and no protonated molecular cation $[M + H]^+$ was detected. The formation of $[M - Cl]^+$ was suggested to occur from $[M + H]^+$ through HCl loss. Our observations indicate that the protonated molecular cation is formed in FAB conditions, but its decomposition pattern involves the loss of carbonyls or carbonyls and HX (X = Cl, CN).

The fact that CO loss dominates over the expulsion of other ligands is likely not related to relative bond energies. In the solution chemistry observed for *fac*-$Re(CO)_3(phen)(X)$ complexes, substitution reactions generally occur at the X ligand,[22-24] indicating an higher stability of Re^{I}–CO vs Re^{I}–X bond. Formation of a transient species containing oxidized Re^{II} centers could explain the preferential labilization of the strong back-bonding ligand CO. It has been suggested by Miller et al.[9] that the 3-nitrobenzyl alcohol matrix may act as an oxidative quencher of excited state molecules which can be produced during the FAB sputtering process. This interesting hypothesis is under further investigation in our laboratory.

Binuclear Re(I)–Ru(II) Complexes. The binuclear complexes that have been investigated are $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)]PF_6$ (**5**) $[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)]PF_6$ (**6**) and $[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)]PF_6$ (**7**). The complexes were detected as intact molecular cations $[M - PF_6]^+$ at m/z 917 (**5**, **6**) and 965 (**7**), respectively, where ruthenium and rhenium maintain the oxidation states of 2+ and 1+.

The fragmentation patterns of the $[M - PF_6]^+$ ions, as obtained by MIKE spectra, include all the decompositions observed with the mononuclear species **1**–**4**. They may also be considered, for the most part, representative of the FAB mass spectra of the more extended oligomeric Re(I)–Ru(II) species here described.

Scheme I is a summary of the fragmentations found with **5** and **6**. The lability of the CO ligand is confirmed and the most abundant fragment ions are produced through this decomposition. Together with expulsion(s) of CO the primary channels of fragmentation include the loss of polypyridine neutral ligand. The previously observed[12] preferential expulsion of bpy over phen is confirmed also in this case. No difference in the fragmentation pattern was found for the cyano linkage isomers **5** and **6**. In all cases, in fact, a preferential cleavage of the cyano–ruthenium junction occurs, as shown by detection of $[Ru(bpy)_2(CN)]^+$ or $[Ru(phen)_2(CN)]^+$ for **5**, **6**, or **7**, respectively. These decompositions represent a peculiarity of mixed Re(I)–Ru(II) complexes in that they are not observed with $[(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)]^+$ and $[(NC)Ru(bpy)_2(CN)Ru(phen)_2(CN)]^+$ derivatives.[12] With these cations cleavages of the Ru–CN–Ru bridges begin to be observed only when the ions have suffered multiple HCN + bpy/phen stepwise losses.[12] This fact suggests a lower strength of the bond between bridging cyanide and the ruthenium moiety, probably due to the back-bonding interaction between Re(I) and the CO groups acting as π acceptors.[25]

The formation of ions at m/z 806 and 413 containing the deprotonated moiety –[Ru(bpy – H)]–, via expulsion of HCN is noteworthy. This is consistent with the intramolecular oxidative-addition mechanism proposed by Bursey et al.,[26] where rotation around the 2,2′-(C–C) bond of the bipyridine occurs with oxidative addition via metal insertion into the 3-(C–H) bond and elimination of HCN, as shown in Scheme II. The same mechanism, with expulsion of HF, has been recently proposed for (polypyridyl)-Ru^{II} compounds.[11]

Trinuclear Re(I)–Ru(II) Complexes. The compounds investigated, $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$ (**8**) and $[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$ (**9**) as well as $[(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_2$ (**10**) and the previously described[12] isomeric form $[(NC)Ru(bpy)_2(CN)Ru(bpy)_2(NC)Ru(bpy)_2(CN)](PF_6)_2$, are detected both as singly charged $[M - PF_6]^+$ and as doubly charged $[M - 2PF_6]^{2+}$ species. An example of the decompositions observed with the singly charged ions is given in Figure 1, for compound **8**. Losses of neutral ligands are the preferential channels of fragmentation; however the ion at m/z 917 is formed through a different process consisting in the cleavage of the Ru–CN bridge with the expulsion of the $[Ru(bpy)_2(CN)]PF_6$ neutral moiety, similarly to what was previously observed for the dinuclear species. To confirm the identity of the resulting fragment $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)]^+$ (m/z 917), its MIKE spectrum was recorded and found to be nearly identical to that shown in Scheme I for the dinuclear complex **5**.

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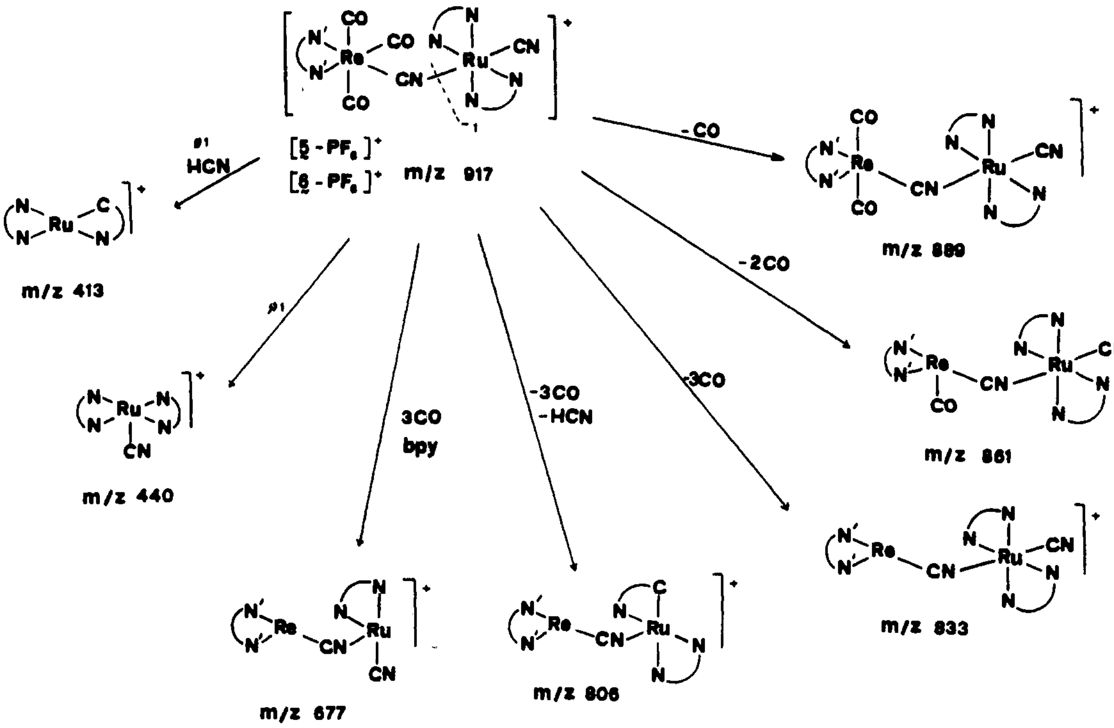
Table I. Fragmentation Pattern of $[Re(CO)_3(phen)X + H]^+$ Complexes under FAB, As Outlined by MIKE Experiments

	m/z (rel intens, %)				
	MH^+	$[MH - CO]^+$	$[MH - 2CO]^+$	$[MH - 3CO]^+$	$[MH - 3CO - HX]^+$
$[Re(CO)_3(phen)(CN) + H]^+$	478	450 (100)	422 (15)	394 (9)	367 (6)
$[Re(CO)_3(phen)Cl + H]^+$	487	459 (100)	431 (18)	403 (12)	367 (3)

Scheme I. Decomposition Pattern of $[M - PF_6]^+$ Ions for the Isomeric Compounds **5** and **6**



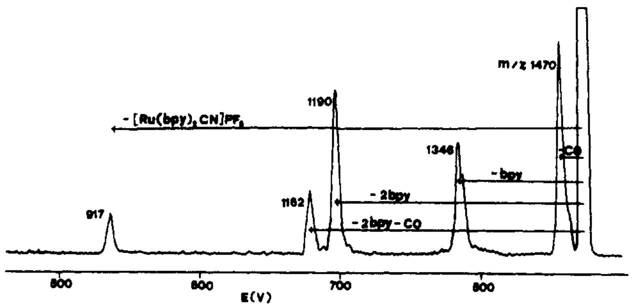
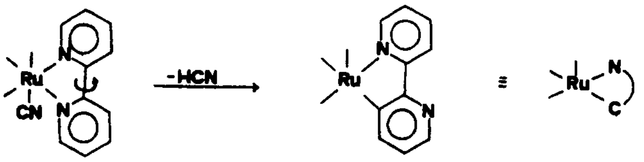


Figure 1. MIKE spectrum of $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)^+$ (m/z 1502) originating from FAB of compound **8**.

Scheme II



The loss of two counterions produces the doubly charged ionic species $[8 - 2PF_6]^{2+}$ and $[9 - 2PF_6]^{2+}$ at m/z 678.5 and 702.5, identified as ions occurring with half mass separation at the expected abundances in the isotopic cluster. The relative abundances of these ions are fairly high, compared with that of singly charged species, as reported in Table II. The MIKE spectrum of the doubly charged intact cation $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)]^{2+}$ is shown in Figure 2. The decompositions follow the usual pattern except for the cleavage of the CN–Ru bridge, not obsteved with these doubly charged ions. This point will be discussed in more detail later.

Quadrinuclear Re(I)–Ru(II) Complexes. The two compounds analyzed, $[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_3$ (**11**) and $[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_3$ (**12**), are detected as singly charged species by elimination of PF_6^-, as doubly charged species by loss of two counterions and as triply charged ions $[M - 3PF_6]^{3+}$. The decomposition patterns of the monocations $[11 - PF_6]^+$ and $[12 - PF_6]^+$, occurring at m/z 2135 and 2087, are rather unexceptional with losses of CO, bpy and both these neutral ligands.

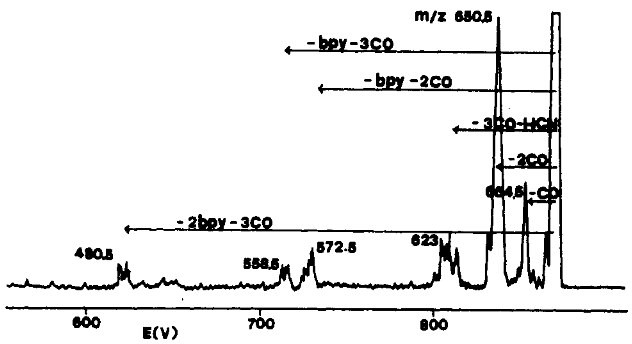


Figure 2. MIKE spectrum of $[Re(CO)_3(phen)(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)]^{2+}$ (m/z 678.5) originating from FAB of compound **8**.

Table II. Relative Abundances (%) of Singly vs Doubly Charged Ions and of Singly Compared with Doubly and Triply Charged Ions Originated from FAB of Compounds **8–10** and **11–12** (m/z Values in Parentheses)

compd	$[M - PF_6]^+$	$[M - 2PF_6]^{2+}$	$[M - 3PF_6]^{3+}$
8	100 (1502)	80 (678.5)	
9	100 (1550)	90 (702.5)	
10	100 (1445)	90 (673)	
11	100 (2135)	60 (995)	10 (615)
12	100 (2087)	50 (971)	15 (599)

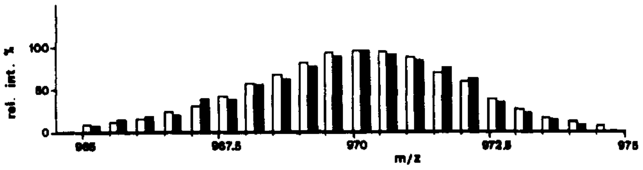


Figure 3. Comparison of isotopic abundances for the theoretically calculated (blank bar) and the experimentally found (solid bar) cluster of $[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)^{2+}$.

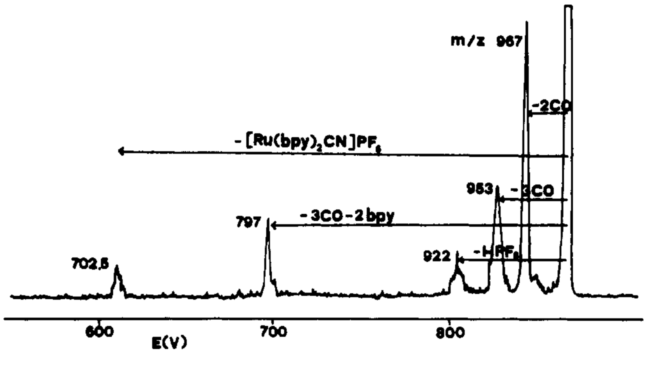


Figure 4. MIKE spectrum of $[Re(CO)_3(phen)(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)^{2+}$ (m/z 995) originating from FAB of complex **11**.

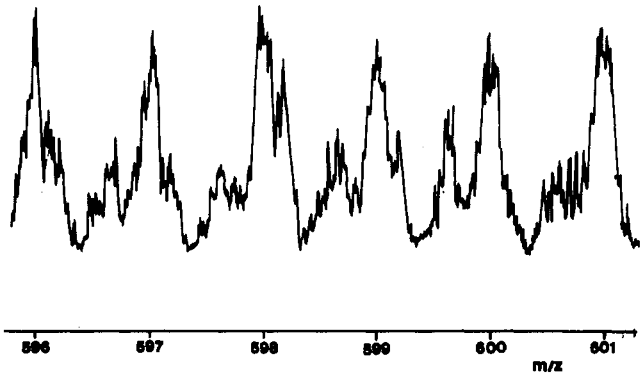


Figure 5. FAB mass spectrum of $[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)](PF_6)_3$ from m/z 596 to 601.

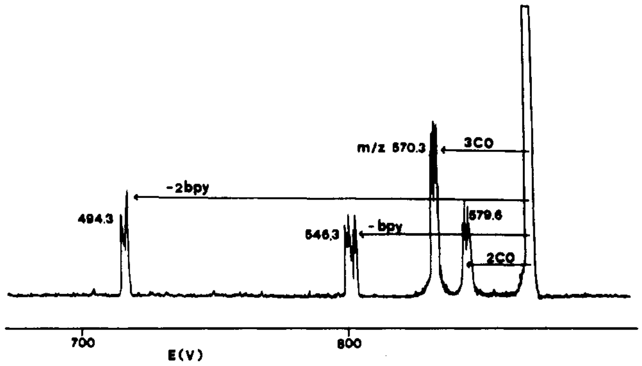


Figure 6. MIKE spectrum of $[Re(CO)_3(phen)(NC)Ru(bpy)_2(CN)Ru(bpy)_2(CN)Ru(bpy)_2(CN)]^{3+}$ (m/z 598.3) originating from FAB of complex **12**.

The multiply charged ions are detected in high relative abundance, as shown by the data collected in Table II. The doubly charged species at m/z 995 and 971 were recognized by ions with half mass peak separation in the isotopic cluster. The observed and calculated isotope distributions are in good agreement for most ion fragments, as shown in Figure 3. An example of unimolecular fragmentations of these doubly charged species is given in Figure 4 for the precursor ion $[\mathbf{11} - 2PF_6]^{2+}$. The major decompositions always include CO losses, partially associated with the expulsion of bpy neutral ligand. The elimination of the third counterion occurs through two different fragmentations: loss of HPF_6 with the proton coming from one of the bipyridine ligands with a mechanism similar to that proposed in Scheme II, or expulsion of a $[Ru(bpy)_2(CN)]PF_6$ neutral moiety, resulting from the decomposition of a CN–Ru bridge.

An interesting observation in this study is represented by the detection of triply charged ions $[M - 3PF_6]^{3+}$ at m/z 615 and 599, respectively. Figure 5 shows a portion of the FAB spectrum of compound **12**, where the triply charged ionic specied can be clearly identified as cluster of peaks appearing at one-third Dalton peak separations. With these data, however, a comparison between the theoretical isotopic cluster and the observed relative abundances is very difficult, due to the overlapping of the background. For this reason the MIKE spectra of the triply charged species has been obtained from ions centered at m/z 614.3 for **11** and 598.3 for **12**, that is in mass spectrum regions lacking interferring peaks. Figure 6 shows the MIKE spectrum of the triply charged ion $[\mathbf{12} - 3PF_6]^{3+}$. The observed decompositions follow the usual trend with losses of carbon monoxide and neutral bipyridine. Noteworthy also in this case is the absence of ions formed through the cleavage of the CN–Ru bridge with elimination of an uncharged Ru(II) compound, cleavage that is detected only when at least one PF_6^- is still present in the ion. Accordingly, the unimolecular CN–Ru bridge decomposition occurs with $[\mathbf{8} - PF_6]^+$, $[\mathbf{9} - PF_6]^+$, $[\mathbf{11} - PF_6]^+$, $[\mathbf{11} - 2PF_6]^{2+}$, $[\mathbf{12} - PF_6]^+$ and $[\mathbf{12} - 2PF_6]^{2+}$ while is not detected with $[\mathbf{8} - 2PF_6]^{2+}$, $[\mathbf{9} - 2PF_6]^{2+}$, $[\mathbf{11} - 3PF_6]^{3+}$ and $[\mathbf{12} - 3PF_6]^{3+}$. This suggests that PF_6^- plays a role in the fragmentation pattern of these ions thus confirming the non-innocence of the counterions in the gas-phase chemistry of many metal complexes. Recent examples include a F^- transfer from the outer-sphere PF_6^- to an inner-sphere coordination site to explain[11,27] the formation of $[Ru(bdmt)(bpy)_2F]^+$ ions from $[Ru(bdmt)(bpy)_2PF_6]^+$ and the insertion of Cl^- coming from ClO_4^- in the decomposition of $Ru(bpy)_3(ClO_4)_2$ to $[Ru(bpy)_2Cl]^+$.[28]

In the present case the lack of observation of fragment ions containing the fluoride group rules out the outer-sphere–inner-sphere mechanism, suggesting a different role of the counterion. Coulombic attraction that retains the PF_6^- on the leaving metal complex $[Ru(bpy)_2(CN)]PF_6$, favoring its expulsion appears to be reasonable.

Conclusions

FAB mass spectrometry of a series of cyano-bridged Re(I)–Ru(II) polypyridine compounds has been described and discussed, confirming the usefulness of this technique in the characterization of the transition metal compounds and in the determination of the fragmentation pathways.

The production of abundant doubly and triply charged ions have been observed using 3-nitrobenzyl alcohol as matrix and their unimolecular decomposition processes have been studied in detail by mass-analyzed kinetic energy spectra. The predominant fragment ions in the MIKE spectra are due to losses of CO and polypyridine neutral ligands. The expulsion of HCN, observed in some cases, can be explained by the intramolecular oxidative-addition mechanism to form a carbon-bound metallocarbacycle.

The unimolecular decomposition processes confirm the minor role played by the charge in the chemistry of these compounds and prove the high stability of the cyano-bridged polynuclear Re(I)–Ru(II) compounds.

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