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Fast Atom Bombardment and Field Desorption Mass Spectrometry of Organometallic Derivatives of Ruthenium(II) and Osmium(II)

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The fast atom bombardment (FAB) and field desorption (FD) mass spectrometric analysis of 18 involatile, cationic organometallic derivatives of 2,2′-bipyridine (bpy) complexes of Ru(II) and Os(II) containing η²-alkene, η²-alkyne, carbonyl, alkyl, and hydrido ligands is presented. Field desorption (FD) and fast atom bombardment (FAB) mass spectrometry are used in concert. In the area of (polypyridyl)metal complex chemistry, these techniques are powerful structural tools; the former gives information on the intact cation, and the latter, fragmentations characteristic of the ligands. The fragmentations can be interpreted on a chemical basis by invoking four concepts: redox fragmentation of metal–ligand bonds, i.e., homolytic dissociation; the simple loss of neutral ligands, depending upon their thermal lability; intramolecular, oxidative addition of coordinated bpy; reductive elimination of HX (X = Cl, H, alkyl).

Introduction

The use of new mass spectrometric techniques as tools for the characterization of organometallic complexes of low volatility has developed rapidly during the last several years. Specifically, field desorption (FD) mass spectrometry[1-4] has been applied in a variety of studies to yield parent ion molecular weight data, although in most instances very little fragment ion information is obtained. Fast atom bombardment (FAB) mass spectrometry,[5,6] although only applied in a few cases, promises to be extremely valuable: parent ion and fragmentation data are exhibited for most samples.[7-10] One of the challenges to be met in utilizing FAB is to relate the fragmentation patterns produced to the structures of the unknown organometallic complex, i.e., to identify the major fragmentation pathways. Given our recent success in applying FAB to a series of coordination complexes and in interpreting the fragment ions in terms of the complexes' thermal chemistry, an obvious extension is to organometallic complexes.

In this paper we present primarily FAB spectral studies but, where appropriate, give complementary FD data, for a series of 2,2′-bipyridine (bpy) organometallic derivatives of Os(II) and Ru(II). The organometallic moieties in our studies are η²-alkene, η²-alkyne, η⁶-benzene, η⁵-cyclopentadienyl, carbonyl, alkyl, and hydride ligands.

The results presented here are extremely encouraging with regard to the use of these spectroscopies in a complementary fashion for characterization of the molecular weight (parent ion mass) of unknown involatile organometallic species, especially cations. Generally, when FAB was unable to provide parent ion information, FD was able to do so. In addition, we will demonstrate that the FAB fragmentation patterns can be interpreted by a combination of simple bond-cleavage processes and redox events.

Experimental Section

Instrumentation. Field Desorption. A Du Pont 21-492B mass spectrometer modified for field desorption was used in this study. The instrument was operated at a 3-kV accelerating potential, and the cathode was held at −7 kV. Samples were dissolved in methylene chloride and placed on the emitter dendrites by the dipping method. Cobalt dendrites were used; their preparations have been described elsewhere.[11] Heating currents of 15–30 mA were sufficient to desorb the samples. The source was maintained at ambient temperature.

Fast Atom Bombardment. A VG 7070 mass spectrometer equipped with a standard VG data system was used in the FAB experiments. The instrument was fitted with a modified saddle field ion source obtained from Ion Tech Ltd. to serve as the atom beam gun. Xenon was used to produce the primary beam. A primary current of 1 mA at an energy of 4–8 KeV provided good sample ion intensities. A stainless-steel probe tip was covered with a small piece of aluminum foil to provide a clean surface for each sample. The sample was placed onto the foil as either a solution or suspension in glycerol. In cases where low solubility in this glycerol matrix seemed to result in poor spectral quality, the sample was first dissolved in a small amount of dimethylformamide. This solution was then placed on the probe with a small amount of glycerol. This enabled us to obtain spectra of previously intractable complexes.

Samples. The carbonyl complexes [Ru(bpy)₂(CO)X](PF₆) (X = H, Cl) and [Os(bpy)₂(CO)X](PF₆) (X = H, Cl, CF₃, CF₃CO₂) were prepared by published techniques.[12] The synthesis of the complex Ru-(η²-C₅H₅)(bpy)Cl will be described in a forthcoming publication.[13] The

(1) Beckey, H. D. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 500–503.
(2) Games, D. E.; Gower, J. L.; Gower, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1980**, *193*, 229–234.
(3) Games, D. E.; Gower, J. L.; Kane-Maguire, L. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1994–1996.
(4) McEwen, C. N.; Ittel, S. D. *Org. Mass Spectrom.* **1980**, *15*, 35–37.
(5) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 345–327.
(6) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *Nature (London)* **1981**, *293*, 270–275.
(7) Tkatchenko, I.; Neibecker, D.; Fraisse, D.; Gomez, F.; Barofsky, D. F. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 499–502.
(8) Johnstone, R. A. W.; Lewis, I. A. S. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 451–454.
(9) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *Biomed. Mass Spectrom.* **1981**, *18*, 491–495.
(10) Miller, J. M. *J. Organomet. Chem.* **1983**, *249*, 299–302.

(11) Bursey, M. M.; Rechsteiner, C. E., Jr.; Youngless, T. L.; Fraley, D. F.; Sammons, M. C.; Hass, J. R. *Adv. Mass Spectrom.* **1978**, *7*, 932–938.
(12) (a) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Organometallics* **1983**, *2*, 551–554. (b) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Ibid.* **1984**, *3*, 1241.

Table I. Major Ions Observed in the FAB Spectra of Hydrocarbon–Ligand (L) Complexes of Ru(II) and Os(II)

| | | *m/z* (rel intens)[a] | | | |
cation[b]	M[+] [c]	(M – L)[+]	(M – Cl)[+]	(M – L – HCl)[+]	other peaks
[Os(bpy)$_2$(η^2-CH$_2$=CH$_2$)Cl]$^+$	567 (13)	539 (164)	...	503 (100)	
[Os(bpy)$_2$(η^2-PhCH=CH$_2$)Cl]$^+$	693 (15)	539 (123)	...	503 (100)	382 (100)[d]
[Os(bpy)$_2$(η^2-CH$_3$CH$_2$C≡CCH$_2$CH$_3$)Cl]$^+$	621 (96)	539 (182)	...	503 (100)	
[Os(bpy)$_2$(η^2-PhC≡CCH$_2$CH$_3$)Cl]$^+$	...	539 (192)	...	503 (100)	473 (50)[e]
[Os(bpy)$_2$(η^2-CH$_3$CO$_2$C≡CCO$_2$CH$_3$)Cl]$^+$	681 (35)	539 (89)	...	503 (100)	647 (103)[f]
[Ru(η^6-C$_6$H$_6$)(bpy)Cl]$^+$	371 (15)	...	336 (100)	...	
Ru(η^5-C$_5$H$_5$)(bpy)Cl	...	...	323 (100)	...	

[a] Relative to (M – L – HCl)$^+$. [b] All PF$_6^-$ salts. [c] M$^+$ defined as the intact cation. [e] Not identified. [f] *m/z* corresponds to (M – Cl + H)$^+$.
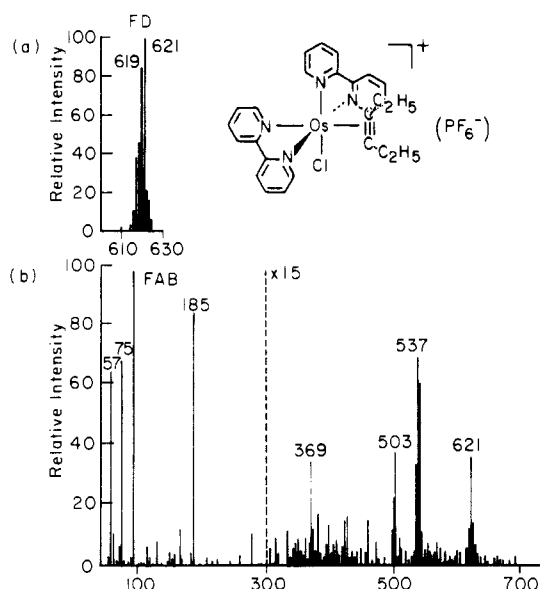

Figure 1. Positive ion mass spectra of [Os^{II}(bpy)$_2$(3-hexyne)Cl](PF$_6$): (a) by field desorption; (b) by fast atom bombardment.

complex [Ru(η^6-C$_6$H$_6$)(bpy)Cl](PF$_6$) was prepared in a manner similar to that described by Stephenson.[14] The ferrocene complex [Ru(bpy)$_2$-(PPh$_2$fc)Cl](PF$_6$) was prepared, isolated, and characterized by methods that have been published for the simple phosphine analogues.[15] General details of the preparation and properties of the alkene and alkyne complexes of Os(II) have been recently described.[16] The details of the preparation and reactions of the alkyl complexes [M(bpy)$_2$(CO)R](PF$_6$) (M = Os, R = CH$_2$Ph; M = Ru, R = CH$_2$Ph and CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$) have been published.[17]

Results and Discussion

π-Bonded Hydrocarbon Complexes. A series of related [Os-(bpy)$_2$(L)Cl](PF$_6$) complexes, where L = ethylene, styrene, 3-hexyne, 1-phenylpropyne, and dimethyl acetylenedicarboxylate (DMAC), were analyzed by FAB and FD to determine the applicability of the techniques to π-bonding ligand groups. For example, of the positive results obtained, the spectra of the 3-hexyne analogue are shown in Figure 1. The FD spectrum contains a cluster of peaks for the complex cation, M$^+$ (*m/z* 621 for the most abundant isotope, ^{192}Os). There are no other peaks in the spectrum. The FAB spectrum also contains small peaks for the complex cation and two useful fragment ions, *m/z* 539 for (M – hexyne)$^+$ and *m/z* 503 for (M – hexyne – Cl)$^+$.

(13) A reviewer suggests that the lower abundance of intact parent ions could be due to a greater number of degrees of freedom for the alkyne complexes resulting in more extensive fragmentation. This issue will have to be resolved in a separate study.

(14) Robertson, D. R.; Robertson, I. W.; Stephenson, T. A. *J. Organomet. Chem.* **1980**, *202*, 309.

(15) Sullivan, B. P., Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334–3342.

(16) Sullivan, B. P.; Kober, E. M., Meyer, T. J. *Organometallics* **1982**, *1*, 1011, 1014.

(17) Sullivan, B. P.; Smythe, R. S.; Kober, E. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4701–4703.

Table I summarizes the results obtained for the FAB analysis on the series of π-bonding hydrocarbon ligands. The *m/z* values given correspond to the species containing the principal isotope ^{192}Os, and the reported intensities are related to the (M – hydrocarbon – X)$^+$ ion for ease in comparison of results.

The M$^+$ ion is observable in four out of the five examples, but only for L = CH$_3$CH$_2$C≡CCH$_2$CH$_3$ and DMAC is it of appreciable intensity. Generally, the most intense fragment is derived by loss of the hydrocarbon substituent as shown in eq 1; in the equation the asterisk denotes a highly vibrationally excited precursor.
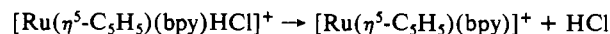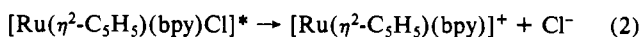
$$[Os(bpy)_2(\pi\text{-hydrocarbon})Cl]^{+*} \rightarrow$$
$$[Os(bpy)_2Cl]^+ + \text{hydrocarbon} \quad (1)$$
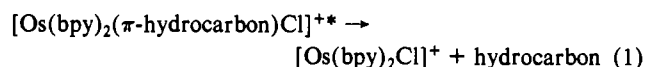
A notable exception to the above intensity rule is provided by [Os(bpy)$_2$(DMAC)Cl]$^+$. While the complex the complex exhibits an intense ion for loss of hydrocarbon, its base peak is as (M – Cl + H)$^+$. As has been shown previously, the glycerol matrix is a source of protons to protonate metal complexes.[18] The absence of an (M – Cl + H)$^+$ ion from the spectra of the other alkene or alkyne complexes implies that protonation occurs initially at the oxygen atoms of the DMAC ligands. Since a protonated DMAC ligand would be unstable with respect to both displacement from the metal and solvolysis of the ester bond by glycerol, a more likely possibility for the structure is the rearrangement fragment **1**.
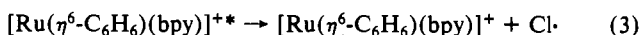

1
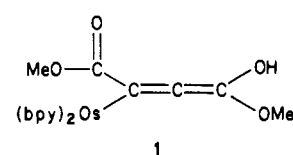
A σ-bonded carbon structure such as **1** should behave much like the Os(II) and Ru(II) alkyl complexes discussed later, where the alkyl group is retained in the fragment ions.

All of the [Os(bpy)$_2$(L)Cl]$^+$ complexes in Table I exhibit a strong peak at *m/z* 503, corresponding to (M – L – HCl)$^+$. This fragment ion, [Os(bpy)$_2$ – H]$^+$, will be discussed below.

The complexes [Ru(η^6-C$_6$H$_6$)(bpy)Cl](PF$_6$) and Ru(η^5-C$_5$H$_5$)(bpy)Cl have very simple spectra. For Ru(η^2-C$_5$H$_5$)(bpy)Cl no parent ion peak is found, and the formal loss of Cl$^-$ is the base peak (eq 2). This peak may also arise by loss of HCl after protonation by solvent.

$$[Ru(\eta^2\text{-}C_5H_5)(bpy)Cl]^* \rightarrow [Ru(\eta^2\text{-}C_5H_5)(bpy)]^+ + Cl^- \quad (2)$$

$$[Ru(\eta^5\text{-}C_5H_5)(bpy)HCl]^+ \rightarrow [Ru(\eta^5\text{-}C_5H_5)(bpy)]^+ + HCl$$

The spectrum of the arene complex contains a peak for intact cation and also one for a fragment due to chlorine loss (eq 3).

$$[Ru(\eta^6\text{-}C_6H_6)(bpy)]^{+*} \rightarrow [Ru(\eta^6\text{-}C_6H_6)(bpy)]^+ + Cl\cdot \quad (3)$$

Chlorine is lost as a radical; this is the common ion fragmentation pathway observed for gas-phase ions from organic halides in mass spectrometry.[19] The process represents a formal reduction of Ru

(18) Cerny, R. L.; Sullivan, B. F.; Bursey, M. M.; Meyer, T. J. *Anal. Chem.* **1983**, *55*, 1954–1958.

Table II. Major Ions in the FAB Spectra of Carbonyl-Chloro and Carbonyl-Carboxylato Complexes of Os(II) and Ru(II), [M(bpy)$_2$(CO)X](PF$_6$)

	m/z (rel intens based on M(bpy)$_2$$^+$)				
cation	M$^{+\,a}$	[M – X]$^+$	[M – CO]$^+$	[MH – X – CO]$^+$	other peaks
[Ru(bpy)$_2$(CO)Cl]$^+$	477 (60)	442 (29)	449 (55)	413 (100)	257 (94)^e
[Os(bpy)$_2$(CO)Cl]$^+$	567 (135)	⋯	539 (87)	503 (100)	381 (59)^f
[Ru(bpy)$_2$(CO)O$_2$CH]$^+$	487 (32)	443 (23)^b	458 (8)^d	413 (100)	257 (71)^e
[Os(bpy)$_2$(CO)O$_2$CH]$^+$	577 (177)	531 (69)^c	⋯	503 (100)	
[Os(bpy)$_2$(CO)O$_2$CCF$_3$]$^+$	645 (127)	⋯	617 (56)	503 (100)	

^{a} Intact cation. ^{b} [M – X + H]$^+$. ^{c} [M – X – H]$^+$. ^{d} [M – CO – H]$^+$. ^{e} [Ru(bpy) – H]$^+$. ^{f} [Os(bpy)Cl – 2H]$^+$.

Table III. Major Ions Observed in the FAB Spectra of Carbonyl-Alkyl and Carbonyl-Hydride Complexes of Os(II) and Ru(II), [M(bpy)$_2$(CO)R](PF$_6$)

	m/z (rel intens based on M(bpy)$_2$$^+$)				
cation	M$^{+\,a}$	[M – R]$^+$	[M – CO]$^+$	[M – R – CO – H]$^+$	other peaks
[Ru(bpy)$_2$(CO)((CH$_2$)$_4$CH$_3$)]$^+$	513 (164)	⋯	⋯	413 (100)	325 (79)^d 257 (90)^e 356 (52)
[Ru(bpy)$_2$(CO)CH$_2$Ph]$^+$	533 (238)	443 (33)^b	⋯	413 (100)	349 (126)^f 257 (100)
[Ru(bpy)$_2$(CO)CD$_2$Ph]$^+$	535 (39)	⋯	⋯		351 (95)^f 257 (69)^f
[Os(bpy)$_2$(CO)CH$_2$Ph]$^+$	623 (188)	531 (61)^c	⋯	503 (100)	257 (69)^e
[Os(bpy)$_2$(CO)H]$^+$	533 (97)	⋯	⋯	503 (100)	

^{a} Intact cation. ^{b} [M – R + H]$^+$. ^{c} [M – R – H]$^+$. ^{d} Unknown. ^{e} [M – (bpy) – R – CO – H]$^+$. ^{f} [M – bpy – CO]$^+$.

and oxidation of Cl$^-$ and is another example of redox fragmentation similar to earlier examples presented for coordination complexes.[18]

An interesting example of how FAB can be applied to systems of some molecular complexity is provided for the bimetallic species [Ru(bpy)$_2$(PPh$_2$Fc)Cl](PF$_6$) (where Fc is a ferrocenyl substituent). The major ions observed in the FAB spectrum of this complex are the intact molecular cation at m/z 819, (M – PPh$_2$Fc)$^+$ at m/z 449, and (M – PPh$_2$Fc – Cl)$^+$ at m/z 412. Ions are also seen that can be related to the phosphine ligand itself: the intact ligand at m/z 370 and PPhFc$^+$ at m/z 293.

Carbonyl-Chloro and Carbonyl-Carboxylato Complexes. Table II contains FAB results for a series of complexes [M(bpy)$_2$-(CO)X]$^+$ (M = Ru(II), Os(II); X = Cl, OC(O)H, OC(O)CF$_3$). The m/z values correspond to the principal isotope of the metal, and the relative intensities are based on the [M – X – CO]$^+$ ion. Unlike the spectra of the hydrocarbon complexes, the parent ions were always present and were generally intense. The major fragmentation pattern always includes CO loss (eq 4). As shown

$$[M(bpy)_2(CO)X]^{+*} \rightarrow [M(bpy)_2X]^+ + CO \qquad (4)$$

in Table II the (M – X)$^+$ fragment analogous to the product of eq 1 occurs only for [Ru(bpy)$_2$(CO)Cl]$^+$. Curiously, 44, not 45, mass units are lost from [Ru(bpy)$_2$(CO)O$_2$CH]$^+$, and 46 are lost from [Os(bpy)$_2$(CO)O$_2$CH]$^+$. We will return to this small but important point later.

A constant feature of all the spectra presented in Table II is the peak near the expected value for [Me(bpy)$_2$]$^+$. Its mass is consistently low by 1 unit from the expected value. In this regard the spectra are similar to all the other complexes presented in Table I and later in Table III. Another common feature of the mass spectrum of the Ru(II) complexes is a fairly intense peak at m/z 257, the [^{102}Ru(bpy) – H]$^+$ fragment.

Carbonyl-Alkyl and Carbonyl-Hydride Complexes. When obtained for these complexes, FD spectra contain only peaks (including isotopes) for the intact cation. The FAB spectra (Table III) contain peaks for the intact cation and useful fragment ions.

In the FAB spectrum of [Ru^{II}(bpy)$_2$(CO)(CH$_2$Ph)](PF$_6$),[16] the peak at m/z 443 corresponding to [M – R + H]$^+$ is perhaps formed analogously to the [M – X + H]$^+$ of the Ru^{II} formate

Scheme I. Fragmentation of cis-[Me(bpy)$_2$(L)X]$^+$ Complexes under FAB^a
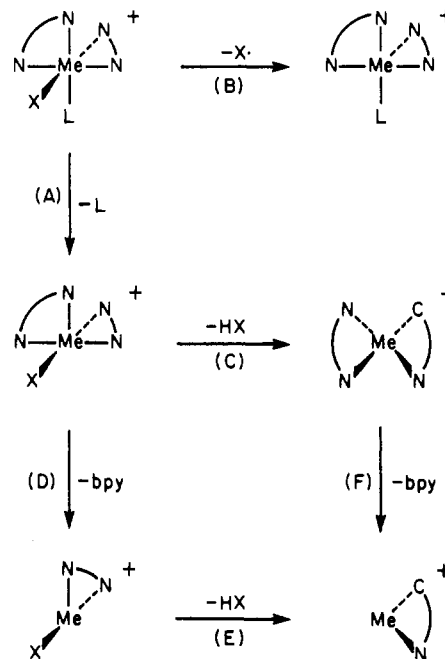
^{a} NN = bipyridyl bound by nitrogens; CN = (bpy – H) bound by C and N as in 2.

complex of Table II. Like all the previously presented Ru(II) complexes, it forms m/z 413 [Ru(bpy)$_2$ – H]$^+$. The [M – (bpy) – CO]$^+$ ion is particularly intense. Similar fragments were observed for the osmium analogue, [Os(bpy)$_2$(CO)(CH$_2$Ph)]$^+$, the major exception being [M – R – H]$^+$ at m/z 531. This ion is also analogous to the behavior of the Os formate complex (Table II), which forms [M – X – H]$^+$.

The spectrum of the deuterated benzyl complex [Ru(bpy)$_2$-(CO)(CD$_2$Ph)]$^+$ supports these ion compositions. Ions retaining the benzyl group have masses 2 units higher than in the unlabeled complex; where it is lost, they have the same mass.

Also in Table III are spectra of the unexceptional compound, the n-pentyl derivative [Ru(bpy)$_2$(CO)((CH$_2$)$_4$CH$_3$)]$^+$ and the hydrido-carbonyl [Os(bpy)$_2$(CO)H]$^+$, which produce intact M$^+$

(19) McLafferty, F. W. In "Interpretation of Mass Spectra", 2nd ed.; W. A. Benjamin: Reading, MA, 1973; p 172.

peaks and, like the others, $[M - R - CO - H]^+$ ions.

Relationship between the Thermal Chemistry of the cis-[M-(bpy)$_2$(L)X]$^+$ Complexes and Their FAB Mass Spectral Fragmentation Patterns. Because of the wide variety of complexes studied and the basic similarity of the fragment ions formed, a rather detailed view of the fragmentation pathways can be offered that is supported by the known solution chemistry of these species. Scheme I in a rather general way summarizes the relevant chemistry involved for the complexes of the type cis-[M(bpy)$_2$-(L)X]$^+$. The structures are not meant to imply stereochemical information but to provide a pictorial representation of the chemistry involved.

In 15 out of 17 examples, a peak corresponding to the formulation [Me(bpy)$_2$(L)X]$^+$ is observed. When the relative intensities of the intact cations [Os(bpy)$_2$(CO)Cl]$^+$ and [Os-(bpy)$_2$(η-hydrocarbon)Cl]$^+$ are compared, all the hydrocarbon species have weaker M^+ peaks. This behavior directly parallels the thermal displacement chemistry of these ligands. For example, the displacement reaction shown in eq 5[12] occurs under conditions

$$[Os(bpy)_2(L)Cl]^+ + CH_3CN \rightarrow$$
$$[Os(bpy)_2(CH_3CN)Cl]^+ + L \quad (5)$$
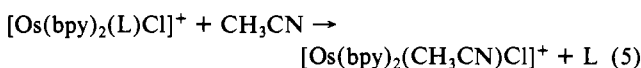
of gentle reflux for L = styrene but not at all for L = CO. Thus, the probability of the pathway marked A in Scheme I, and therefore the relative intensity of M^+ in the spectrum, reasonably depends on the thermal ability of L.[12] The product of A is the ion $(M - L)^+$.

Pathway B in Scheme I is the formal loss of X: that is, an alkyl, hydrogen, chlorine, or carboxyl radical. This is an example of redox fragmentation; in these examples formal Ru(I) or Os(I) is produced. From Table I when L is a labile ligand like an alkene or alkyne, this pathway is shut off. Only in the case of [Ru-(bpy)$_2$(CO)Cl]$^+$ is the intensity of this ion appreciable.

The most consistently present ion and usually one of the most intense in the spectra is the $[M(bpy)_2 - H]^+$ ion (m/z 413 for Ru; m/z 503 for Os). In our previous study of bipyridyl complexes containing Re, the fragments containing bpy generally have the appropriate mass.[18] This lack of analogy argues for a different chemical process that occurs in the Ru and Os complexes discussed above. This process could involve the production of a cyclometalated bpy ligand, an example of which has been characterized by X-ray crystallography in Ir–bpy chemistry.[20]

Given this chemical precedent and the ability of coordinatively unsaturated Ru(II) and Os(II) complexes to undergo intramolecular oxidative-addition reactions to form, for example, "ortho-metalated" phenylphosphine derivatives, structure **2** is reasonable for the $[Me(bpy)_2 - H]^+$ fragment. The entire fragmentation scheme for $[M(bpy)_2(L)Cl]^+$ complexes is consistent with these carbon-bound bpy substituents.
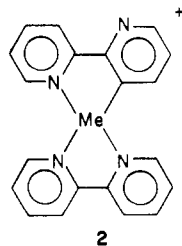

2

Pathway C in Scheme I is a possible sequence for the production of the carbon-bound bpy metal fragment by rotation around the carbon–carbon bond between the two aromatic rings and elimination of an HX molecule.

Pathway D results in a $[Me(bpy)X^+]$ fragment by simple loss of bpy from the intermediate $[Me(bpy)_2X]^+$ species and is thus in competition with the formation of the carbon-bound $[Me(bpy)_2 - H]^+$ fragment. The $[Me(bpy)X]^+$ species is observed for both Ru and Os in several cases in Tables I–III.

(20) Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. *J. Chem. Soc., Chem. Commun.* **1981**, 1284–1285.

Scheme II. Fragmentation of Carbonyl–Benzyl–Bipyridyl Complexes and Carbonyl–Formato–Bipridyl Complexes^a
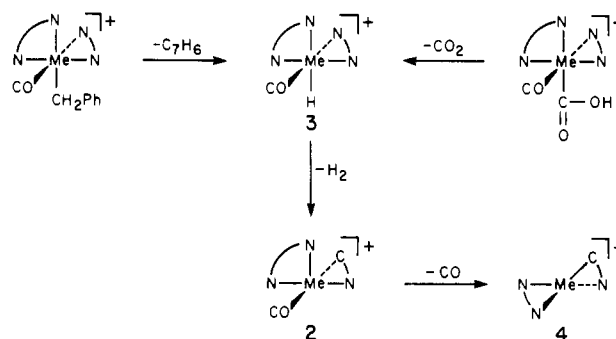
^{a} NN = bipyridyl bound by nitrogens; CN = (bpy – H) bound by C and N as in **2**.

Table IV. Isotopes of the Complex $[Ru^{II}(bpy)_2(CO)Cl]^+$ and Comparison of Relative Isotopic Intensities by Theory, by Field Desorption, and by Fast Atom Bombardment

	rel isot intens		
m/z	theor	FD	FAB
471	13	21	13
472	3	5	
473	12	16	5
474	34	38	45
475	40	48	42
476	60	61	71
477	100	100	100
478	34	28	34
479	76	74	98
480	16	15	18
481	16	12	11
482	3	4	

Finally, both pathways E and F result in the formation of the $[Me(bpy) - H]^+$ carbon-bound fragment. This fragment is not of significant intensity for the $[Os(bpy)_2(\pi$-hydrocarbon)Cl]$^+$ complexes but otherwise is significant.

Although the fragmentation patterns of most of the complexes can be understood in terms of Scheme I, the complexes [Me-(bpy)$_2$(CO)CH$_2$Ph]$^+$ and [Me(bpy)$_2$(CO)OC(O)H]$^+$ probably fragment by the different route in Scheme II. For the case of Ru, the m/z 443 carbonyl–hydride **3** is observed, but for Os this ion eliminates H_2 concomitant with oxidative addition to yield the cyclometalated bpy fragment **2**. Loss of CO from this fragment gives the ubiquitous $[Me(bpy)_2^+ - H]^+$.

In the spectrum of $[Ru(bpy)_2(CO)CD_2Ph]^+$ the carbonyl deuteride (**2**) is not observed, because the intact cation is much weaker than the intact cation in the proton alalogue.

The solution thermal chemistry of $[Me(bpy)_2(CO)CH_2Ph]^+$ is unknown, but the formate complexes yield the corresponding hydrides by extrusion of CO_2.[12,13] Such observations provide an analogue for the corresponding formation of **3** in Scheme II.

Isotopic Abundances in [Ru(bpy)$_2$(CO)Cl]$^+$ by Field Desorption Mass Spectrometry. The isotopic pattern of a cation can be useful for identification. Many transition metals have several stable isotopes over 10% with natural abundance. If one considers the contribution of minor isotopes, the combination of such a metal with C, N, O, and Br, for example, will have an isotopic pattern that can be utilized as a fingerprint to identify the composition.

These desorption processes do not provide a steady sample ion current, in contrast to EI and CI mass spectrometry; instead, the ion current fluctuates. To reduce the effect of this fluctuation on observed relative ion intensities, many scans should be averaged, in order to smooth out irregularities in ion intensities due to bursts of ions. Anticipating these irregularities, one must evaluate how closely experiment follows theory.

Table IV compares the experimental values obtained by FD and FAB of relative isotopic intensities to the theoretical intensities for the cation Ru^{II}(bpy)$_2$(CO)Cl$^+$. The FAB values represent an

average for 16 scans, and the FD values represent an average of eight scans. The experimental intensities for most masses are within 10% (relative) of the theoretical values. Our experience with FD and FAB is that this result is a close match and strong evidence of the composition.

Conclusions and Final Comments. Both FD and FAB mass spectrometry are viable techniques for the analysis and characterization of a wide variety of organometallic complexes.[18] As with the coordination complexes, the two seem to be complementary in nature; FD, a more gentle technique, provides information on the intact complex cation (or, for neutral complexes, the molecular ion), and FAB reveals aspects of the ligands through fragment ions. It is appropriate to use FAB initially, especially because it is easier to use. If the intact complex must be characterized, FD may then be used.

Schemes I and II permit interpretation of the fragmentation patterns of $[Me(bpy)_2(L)X]^+$ complexes and are based on three concepts: the lability of L; the oxidative-addition reaction of bpy to form carbon-bound (bpy – H) ligand; the reductive elimination of HX. Thermally induced FAB reaction chemistry should provide the basis to predict fragmentation patterns of other organometallic species, especially of low-valent, electron-rich metals.

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Electron Spin Resonance Studies of the One-Electron-Reduction Products of Nickel(II) 1,3-Dithio β-Diketonate Complexes

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The ESR spectra of the initial one-electron-reduction products of nickel(II) bis(1,3-dithio β-diketonate), $Ni(SacSac)_2$, have been observed at low temperatures after controlled-potential electrolysis. The spectra are well resolved and at 77 K show anisotropic *g* values, which are intermediate in magnitude between those found in sulfur-containing radical anions and nickel(I) d^9 complexes. In addition hyperfine interaction is observed between the unpaired electron and the four equivalent methyl groups of the SacSac ligand while no coupling is observed to the methine proton. The results are consistent with a ligand-based reduction, the electron entering a ligand p_π molecular orbital with nodes at the 2-carbons. This is in agreement with recently reported INDO calculations of the electronic structure of $Ni(S_2C_3H_3)_2$ and SW–$X\alpha$ calculations reported in this work. In contrast, the one-electron-reduction product of $[Ni(dpe)(SacSac)][BPh_4]$ (dpe = 1,2-bis(diphenylphosphino)ethane) is found to give the unpaired electron in a metal-based molecular orbital as has been found in other mixed-ligand dpe/bidentate sulfur ligand complexes. ESR spectra of the analogous $[Pd(SacSac)_2]^-$ monoanion are less anisotropic but show larger coupling in the perpendicular region of the spectrum to the methyl protons. This is again consistent with a π-type singly occupied molecular orbital (SOMO) similar to that found in the $[Ni(SacSac)_2]^-$ monoanion.

Introduction

Electrochemical methods such as cyclic voltammetry and other controlled-potential techniques allow the ready investigation of the redox properties of transition-metal complexes. An attractive feature of these techniques is that we may view the working electrode as adding or removing electrons to or from the solute molecule, to the lowest unoccupied molecular orbital (LUMO) or from the highest occupied molecular orbital (HOMO). However, the detailed electronic nature of the species produced in the electrochemical process is often less well-known; many such species are highly reactive or difficult to isolate and characterize by conventional chemical and structural methods.

Recent studies[1–3] of the redox chemistry of group 8 nickel(II), palladium(II), and platinum(II) complexes of bidentate sulfur and other ligands combined with electron spin resonance spectroscopy have, in the case of one-electron reduction, given information on the LUMO of the complex. In particular it has been possible to decide in many cases whether the unpaired electron is occupying a molecular orbital primarily localized on the metal atom leading to a d^9 monovalent, M(I), complex[1] or is delocalized over the ligands to give a divalent radical anion complex.[3] Thus,

the initial one-electron reduction of both bis(dialkydithiocarbamato)nickel(II), $Ni(S_2CNR_2)_2$,[1] and the bis(maleonitriledithiolato)nickel(II) dianion,[2] $[Ni(S_2C_4N_2)_2]^{2-}$, for example have been found to be metal based, leading to the appropriate nickel(I) complex (Figure 1). The singly occupied molecular orbital (SOMO) of b_{1g} symmetry is principally composed of the nickel d_{xy} orbital ($\alpha^2 = 0.8$ for $[Ni(S_2CNR_2)_2]^-$ and $\alpha^2 = 0.7$–0.8 for $[Ni(S_2C_4N_2)_2]^{3-}$) and the sulfur ligand p_σ orbitals.

The electrochemical properties in acetone/tetraethylammonium perchlorate of the analogous 1,3-dithiol ligand complexes[4] (Figure 2), bis(1,3-dithio β-diketonate)nickel(II), were first reported by Bond, Heath, and Martin.[5] They found that the molecule bis(dithioacetylacetonato)nickel(II), $Ni(SacSac)_2$, underwent an initial reversible one-electron reduction, at mercury electrodes, followed by a further chemical reaction (without ligand loss) to a species that was reoxidizable to the neutral $Ni(SacSac)_2$. Geiger and co-workers[6] investigated this reduction using cyclic voltam-

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(1) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K.; Hope, J. M.; Martin, R. L. *Inorg. Chem.* **1982**, *21*, 1152.
(2) Geiger, W. E., Jr.; Allen, C. S.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1977**, *16*, 2003.
(3) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. *Inorg. Chem.* **1982**, *21*, 3565.
(4) Lockyer, T. N.; Martin, R. L. *Prog. Inorg. Chem.* **1980**, *27*, 223.
(5) Bond, A. M.; Heath, G. A.; Martin, R. L. *Inorg. Chem.* **1971**, *10*, 2026.