The Structure of $C_5H_5RFe^+$ ($R = F, Cl, Br, I, O, OH, OCH_3, C_6H_5, H$) Ions in the Gas Phase and the Generation of Their Neutral Counterparts by Neutralization–Reionization Mass Spectrometry

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The structure of $C_5H_5RFe^{++}$ ions was studied by tandem mass spectrometry that included the neutralization–reionization (NR) method. Halogen-containing species ($R = F, Cl, Br, I$) showed fragmentation that was consistent with a structure that has the cyclopentadienyl ring and R as separate ligands at the metal atom (structure A). This structure also was identified for $C_5H_5FeO^+$ and $CpFeOH^{++}$ ions, but these species also easily isomerized to metal-cyclopentadiene structure, $RC_5H_5Fe^{++}$ (B), followed by hydrogen rearrangement(s) and CO loss. B was the dominant structure of $C_5H_5FeH^{++}$ and $C_5H_5FeC_6H_5^{++}$ ions. All ions that have structure A showed recovery signals in their NR mass spectra that indicated that their stable neutral counterparts were generated. The NR mass spectra also provided complementary information about the structure of ions before neutralization and after reionization. (*J Am Soc Mass Spectrom* 1995, 6, 1143–1153)

Non-transition metal derivatives of the type CpMR, where M is a metal atom, Cp is the cyclopentadienyl ring, and R is a σ -ligand, are well known species in the condensed phase. In these complexes the cyclopentadienyl group can be covalently or π -bonded to the central metal atom. Stable π -CpMR complexes of the main group elements, which have a substituted or unsubstituted cyclopentadienyl ligand, have been observed experimentally [1]. Transition metal-containing derivatives of this type never have been isolated. The instability of these species can be explained well by the electron and coordination deficiency of the metal atom. The cyclopentadienyl ring usually is bound to the metal atom as an η^5 ligand, but the remaining radical R cannot provide enough electrons to complete the metal's valence electron shell. To make these species stable, additional ligands or solvent molecules should be attached to the metal atom. For example, many stable complexes of the type $CpFe(CO)_2R$ have been synthesized and characterized. These compounds are potential sources for CpFeR species that, for example, may be formed by

photochemical reactions. However, even in these cases it has proved impossible to isolate pure CpMR species that have no solvent molecules in the coordination sphere of the metal atom.

Neutralization–reionization mass spectrometry (NRMS) has been used recently to generate and characterize elusive and *hitherto* unknown organometallic species [2]. In these experiments the corresponding cations were generated in the gas phase and then neutralized by electron transfer from a target gas. A variety of cyclopentadienyl complexes of transition metals have been examined by this method; most of these complexes showed a recovery signal in their neutralization–reionization (NR) mass spectra, which unequivocally indicates that under these experimental conditions the corresponding neutrals have been produced as stable species.

The aim of the present work was to generate various CpFeR neutral species in the gas phase by using NRMS. Their positively charged precursors were produced by electron impact ionization of the corresponding dicarbonyl complexes $[CpFe(CO)_2R]$. In cases where no stable $CpFe(CO)_2R$ was available ($R = H, F, OMe, O, OH$), $CpFeR^+$ ions were produced by dissociation of ferrocene derivatives of the type $FcXR$ ($Fc = C_5H_5FeC_5H_4$). Metastable ion (MI), collision-induced

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dissociation (CID), and collision-induced dissociative ionization (CIDI [3]) mass spectra of these species were studied to assign structures to the ions.

Experimental

Cyclopentadienyldicarbonyliron iodide was purchased from Aldrich Chemical Co. (Milwaukee, WI). Other $\text{CpFe}(\text{CO})_2\text{R}$ complexes ($\text{R} = \text{Cl}, \text{Br}$) were synthesized by a standard procedure [4]. The synthesis of ferrocene derivatives used as precursors for CpFeR^{++} ions also has been described [5].

Electron impact (EI) mass spectra were recorded via a modified triple sector (BEE) VG ZAB-2F mass spectrometer (VG Analytical, Manchester, UK). The energy of the ionizing electrons was 70 eV, and the temperature of the ion source was 100–120 °C. All samples were introduced into the mass spectrometer via the direct insertion probe heated to 60–100 °C.

MI, CID, CIDI, and NR mass spectra were recorded via the same mass spectrometer, which had two collision cells (CC) in each of the second and third field-free regions (2FFR and 3FFR), by scanning the voltage of the first or second electric sectors. The program ZAB-CAT (Mommers Tech., Vanier, Ontario, Canada) was used for the data acquisition and processing [6]. At least 10 spectra were averaged in each experiment.

Isotope overlapping of ions of interest with other species, which usually contain one or two hydrogen atoms less, was insignificant in all cases except CpFeF^{++} ions. In the latter case intensities of peaks that correspond to $\text{C}_5\text{H}_5\text{FeF}^{++}$ and $\text{C}_5\text{H}_4\text{FeF}^{++}$ ions were similar. Their MI, CID, and NR mass spectra, however, were different. To avoid the contribution of $\text{C}_5\text{H}_4\text{FeF}^{++}$ species in the NR mass spectrum of $\text{C}_5\text{H}_5\text{FeF}^{++}$, the NR experiments with the latter ions, generated from the metastable precursor, were carried out. The NR mass spectra of this and ion source-generated species were similar and contained recovery signals.

Kinetic energy release measurements for metastable ions ($T_{0.5}$) were performed at sufficient energy resolution to reduce the main beam width at half-height to 3–5 V.

Oxygen was used as collision gas in all CID and CIDI experiments. In the CID experiments with ion source-generated ions, the pressure of oxygen in the appropriate CC was adjusted to provide a main beam transmission of 90%, which corresponded to essentially single-collision conditions. In collision experiments with metastable generated ions or survivor ions (after NR), the transmission of the main ion beam was reduced to ~70%. In the latter cases, ions of interest generated in the 2FFR were mass-selected by the second electric sector and transmitted into the 3FFR to be collisionally activated.

Two types of CIDI experiments were performed. In the first, no gas was added in the first CC, which allowed the examination of neutral products of metastable ion dissociations. In the second type, CIDI

(He-O_2), helium was added in the first CC (main beam reduction 5–10%) to analyze neutrals that originated from both metastable and collision-induced dissociations.

In NR experiments dimethylamine and oxygen were used for neutralization and reionization, respectively. The pressure of Me_2NH in the first CC of the corresponding FFR was adjusted to transmit ~50% of the main ion beam, and the pressure of O_2 in the second CC reduced the main ion beam by 20%.

Two procedures were employed to obtain CID mass spectra that had no contribution from metastable ions. In the first, the MI mass spectra were recorded under the same experimental conditions as the CID mass spectra and subtracted from the combined CID-MI mass spectrum. In the second, a potential of 500–1000 V was applied to the cell with collision gas to separate ions that arise from the metastable and collision-induced dissociations. The results of these methods were similar except for small differences in intensities of peaks caused by mass discrimination in the second procedure.

Formation of CpFeR^{++} Ions

Reactions that resulted in CpFeR^{++} ions are shown in Scheme I. CpFeI^{++} , CpFeBr^{++} , and CpFeCl^{++} ions were generated by the electron impact-induced dissociation of the corresponding dicarbonyl complexes [$\text{CpFe}(\text{CO})_2\text{R}$]. Their EI mass spectra have been reported elsewhere [7, 8] and showed CpFeR^{++} ions as the base peak.

Benzoylferrocene was used to obtain CpFePh^{++} ions. In agreement with the data from ref 9, these ions were among the most abundant species in the EI mass spectrum of this compound, where they were produced by $\text{C}_5\text{H}_4\text{CO}$ loss directly from molecular ions [10].

Monosubstituted ferrocene derivatives, which have the corresponding functional group in the substituent and shown in Scheme I, were used as sources for CpFeOH^{++} , CpFeOMe^{++} , and CpFeF^{++} ions. The EI mass spectra of FcCH_2OH [11, 12], FcCOOH [9, 13, 14],

Scheme I

FcCOOMe [9], and FcCOCF₃ [10] have been reported and contained abundant peaks for $CpFeR^{++}$ ions. Their direct formation from the corresponding FcXR derivatives was shown by their presence in the MI mass spectra of these molecular ions.

$C_5H_6Fe^{++}$ ions were produced by the EI-induced dissociation of $CpFeC_5H_4COOMe$, which involved methoxy group migration to the metal atom followed by the consecutive losses of C_5H_4CO and CH_2O . This decomposition has been described in refs 9 and 10.

Nitroferrocene, $FcNO_2$, whose EI mass spectrum was reported in ref 10, was used to generate $CpFeO^+$ ions. Their formation from the molecular ions of this compound was supported by the MI mass spectrum, which showed an abundant peak at m/z 137. $CpFeO^+$ ions also were present in the mass spectra of $CpFeC_5H_4CH_2OH$ and $CpFeC_5H_4COOH$, but their origin and, therefore, structure were uncertain.

The General Approach to the Identification of $CpRFe^+$ Ion Structures

Ions of formula $CpFe^+R$ may exist in several isomeric forms. Consideration of the cyclopentadienyl ring as a cyclic π -ligand, indicates two structures, **A** and **B**, are

the most important species. The structure **A** contains a radical $R^\cdot$ connected to the metal atom, whereas isomer **B** has R bonded to the cyclopentadienyl group. We propose that ions of structure **A** are originally formed from their cyclopentadienyldicarbonyl or ferrocenyl precursors (Scheme I) and the following discussion will rest upon this premise. Ions **B** may or may not be generated from **A**, dependent on the nature of the group R and the experimental conditions.

A priori, structures **A** and **B** are expected to show different unimolecular dissociations. The experimentally observed dissociations of $CpFeR^{++}$ ions are shown in Scheme I. Their MI and CID mass spectra are presented in Table 1.

Some of the reactions shown in Scheme I can reliably be assigned to structures **A** or **B**. For example, the observation of RFe^+ or Cp^+ ions should be ascribed to isomer **A**. The latter ion is associated with the formation of neutral $RFe^\cdot$, and so this will be indicated by the presence of RFe^+ ions in the CIDI mass spectrum.

The most important characteristic of isomer **B** is the observation of CpR^{++} ions. The formation of Fe^{++} ions also may indicate coupling of the cyclopentadienyl and R ligands to produce the **B**-type structure. This however must be supported by the results of CIDI mass

Table 1. Relative abundances of principal ions in MI and CID mass spectra of $CpFeR^+$ ions^a

R		$C_5H_4RFe^+$	$C_5H_3RFe^+$	$C_5H_5Fe^+$	$C_5H_4Fe^+$	RFe^+	$C_3H_3FeR^+$	$C_3H_5Fe^+$	$C_2H_5Fe^+$	Fe^+	$C_5H_5R^+$	$C_5H_5^+$	$C_3H_3^+$
I	MI	—	—	100									
	CID	2	—	68	—	17	—	4	1	6			
Br	MI	—	—	100									
	CID	5	—	25	—	43	—	6	2	10	—	2	
	m*-CID	< 1	—	43	—	40	3	6	1	4	—	< 1	1
	NR-CID	—	—	58	—	31	2	4	< 1	3	—	< 1	1
Cl	MI	—	—	9	—	91							
	CID	2	—	4	2	50	—	3	3	16	—	8	7
	m*-CID	—	—	23	6	48	6	2	< 1	8	—	2	5
	NR-CID	—	—	14	3	68	2	5	—	4	—	2	1
F ^b	MI	35	—	—	43	17	—	1	< 1	1	< 1	3	
	CID	< 1	—	< 1	2	21	5	10	1	16	< 1	13	12
	m*-CID	4	—	< 3	23	21	13	3	4	4	—	7	2
	NR-CID	1	—	—	38	27	5	1	1	5	—	5	5
OH ^c	MI	4	3	—	44	23	—	—	—	2	2		
	CID	2	—	3	4	44	—	10	8	15	—	2	3
	m*-CID	< 1	< 1	14	22	29	2	9	11	9	—	< 1	2
	NR-CID	< 1	1	2	38	25	< 1	6	3	7	—	1	7
H	MI	22	—	(22)	—	—	—	—	—	78			
	CID	38	—	(38)	—	—	—	3	3	48	3	2	1
	m*-CID ^d	40	—	(40)	—	—	—	11	4	29	2	1	1
Ph ^e	MI	4	7	—	—	—	—	—	—	—	86	—	
	CID	1	2	< 1	—	< 1	—	3	2	6	61	< 1	< 1
	m*-CID	—	58	5	—	2	12	2	1	3	12	< 1	

^a Intensities are in percent of the total fragment ion current. For ion precursors, see text. All data are for the second field-free region. Other important ions (their abundances in the MI and the corresponding CID mass spectra are in parentheses).

^b $C_3H_5Fe^+$ (—, 2, 7, 1), CH_3Fe^+ (—, 2, 5, 1).

^c $C_4H_6Fe^+$ (23, < 1, 2, 17), $C_2H_3Fe^+$ (—, 2, 2, 1).

^d For $C_5H_6Fe^{++}$ ions generated from metastable $CpFeOMe^{++}$; $FeC_5H_6^{2+}$ (5).

^e $C_{11}H_9^+$ (—, 7, 2), $C_9H_9^+$ (—, 11, 4).

spectra, wherein the presence of reionized CpFe^{++} species or $\text{C}_5\text{H}_4\text{R}^+$ ions will identify the loss of CpR as a single unit.

Other decompositions, such as hydrogen atom elimination, $\text{R}^\cdot$ and RH losses, may occur from one or both CpFeR^{++} isomers, and it is difficult to assign these processes to isomers prior to experiment. The nature of reactions that involve the loss of other non-metal-containing species will be discussed separately. Nevertheless, some preliminary assignments can be made. The loss of R must occur easily from structure **B** that has a substituted cyclopentadiene ligand (for the decomposition of such complexes see, for example, ref 15). One should remember that the initial form of CpFeR^{++} is structure **A**, which also is capable of losing $\text{R}^\cdot$. The loss of $\text{H}^\cdot$ from the cyclopentadienyl ring is a high energy process and probably will not compete in the metastable ion time frame with metal-ligand bond cleavage reactions in **A**-type isomers. However, collisional activation of CpFeR^{++} ions may well result in this reaction. A hydrogen atom can be lost more easily from the **B** isomer, which contains an allylic H atom. If the energy barrier for $\text{A} \Rightarrow \text{B}$ isomerization is low, then the formation of $\text{RC}_5\text{H}_4\text{Fe}^+$ ions by $\text{H}^\cdot$ loss may be one of the most important reactions of metastable ions.

To study the isomerization and dissociation of CpFeR^{++} ions, experiments with species that have different origins and internal energies were performed. These were: (1) MI mass spectra of CpFeR^{++} ions that have different lifetimes, from ~ 15 to $30 \mu\text{s}$ (for ions that decompose in the 2FFF and 3FFR, respectively), were recorded; (2) CID mass spectra of ion source-generated CpFeR^{++} ions also were recorded in the 2FFR and 3FFR; (3) CID mass spectra of ion source-generated species were compared with those of metastably produced CpFeR^+ ions (m^* -CID) that have low internal energies. CID mass spectra also were measured for ions that survived NR conditions (NR-CID). These ions presumably had higher average internal energy than ion source-generated species.

No systematic studies on kinetic energy releases have been reported for metastable organometallic and, in particular, iron-containing ions. The $T_{0.5}$ values for most metastable decompositions of CpFeR^{++} ions measured in the present work ranged from 30 to 40 meV and the peaks were of noncomplex Gaussian shape and so had no features of special significance for ion structure assignments.

Structures **A** and **B** (or **C**) are expected to show different stabilities under neutralization-reionization conditions. The applications of NRMS to organometallic species recently have been reviewed [2]. Most of the complexes studied by this method, which had π -cyclopentadienyl rings or groups covalently bound to the metal atom, showed abundant recovery signals. Species in which the metal atom has an even-electron ligand, may (for example, FeC_2H_4^+ and FeCO^+ [16]) or may not [$\text{Fe}(\text{C}_2\text{H}_2)_2^+$ and FeC_6H_6^+ [17], etc.] survive

NR conditions. These general observations can be applied to ions of type **A** and **B**. Isomers **A**, which have both the π -cyclopentadienyl ring and σ -ligand bound to the metal atom, likely will exhibit intense recovery signals in their NR mass spectra. The isomer **B** can be considered as a complex between the metal atom (ion) and a neutral organic molecule. Such species are unlikely to produce stable neutral counterparts and may therefore show no recovery signal. The absence of a recovery signal then may be indicative of the presence of a **B**-type or related structure. The interpretation of an NR mass spectrum that contains a weak recovery signal is not an easy task. The peak may result from both the low, but nonzero, stability of the neutral **B** species or from the presence of **A**-type ions. It should be noted that the observation or nonobservation of a recovery signal in an NR mass spectrum also can depend on the experimental conditions, which include the nature of neutralization target, intercell distance, and so forth [2]. Moreover, the present interpretation of NRMS results *does not* permit quantitation of ions that have different structures and physical characteristics; only qualitative arguments by analogy may be applied. The CID mass spectra of recovery ions were measured to help solve the foregoing problem. If the NR-CID mass spectrum was similar to that of the CID mass spectrum of metastably generated ions, it is likely that the survivor ions had structure **A**.

Unimolecular Decomposition of CpFeX^+ Ions

The MI mass spectra of CpFeR^{++} ions that decompose in the 2FFR of the ZAB-2F mass spectrometer are listed in Table 1. The CID mass spectra were corrected by subtracting the contribution from metastable dissociations (see Experimental for details).

CpFeI^{++} , CpFeBr^{++} , and CpFeCl^{++} Ions

The dissociation characteristics of these three species were similar and so the experimental results will be considered together.

The MI mass spectra of CpFeI^{++} and CpFeBr^{++} ions were very simple; they contained only one significant signal, which corresponded to loss of the halogen atom. Trace signals for RFe^+ ions were observed, relative intensity 0.1% or less, but they may well result from collisions with residual gas rather than to true metastable decompositions. The differences in activation energies for the two processes, $\text{Cp}^\cdot$ and $\text{I}^\cdot$ or $\text{Br}^\cdot$ losses, should therefore exceed $\approx 12 \text{ kcal mol}^{-1}$; otherwise they would compete more effectively in the metastable time frame.

The decomposition of metastable CpFeCl^{++} ions also involved halogen atom elimination that resulted in CpFe^+ ion formation. This reaction was, however, no longer the most abundant metastable process, which now arose from the loss of the cyclopentadienyl ring

and produced $ClFe^+$ ions. The difference in the behavior of halogen-containing $CpFeR^{++}$ ions can be explained by an increase in the Fe—R bond strength in going from the heavier to the lighter and more electronegative halogens. This effect will be illustrated further by the results for $CpFeF^{++}$ ions.

The intensities of $CpFe^+$ and RFe^+ ions increased when a collision gas was admitted to the collision cell and the $RFe^+/CpFe^+$ ion abundance ratios increased greatly in the CID mass spectra (Table 1) following the order $R = Cl > Br > I$.

Collision-induced dissociation of the preceding species also involved cyclopentadienyl ring destruction that resulted in $C_3H_3^+$ and $C_3H_4^+$ and C_2H_2 species coordinated to Fe^+ or RFe^+ . Fe^+ ions of variable abundance were formed upon collisional activation. They most likely originated from secondary reactions that involved the decomposition of energy rich $CpFe^+$ and RFe^+ ions and not directly from $CpFeR^{++}$. If the latter reaction took place with a single-step formation of Fe^+ , then $C_5H_5R^{++}$ or $C_5H_4R^+$ ions would be expected in the CIDI and NR mass spectra. None of these species was found, which indicates no $A \Rightarrow B$ isomerization.

One of the collision-induced dissociations of $CpFeR^{++}$ ions was the loss of a hydrogen atom. This reaction originally was considered by us to be indicative of the B-type structure. To explain the origin of $C_5H_4RFe^+$ ions, a triple mass spectrometry experiment was carried out with $(C_5, H_4, Br, Fe)^+$ species, generated in the 2FFR from $CpFeBr^{++}$. The resultant CID mass spectrum showed $C_5H_4Fe^+$ and $BrFe^+$ ions as the most abundant species, with only a small signal due to Fe^+ ions. These results are consistent with the presence of C_5H_4 and Br as separate ligands at the central metal atom. We propose therefore that the foregoing H atom loss occurred from isomer A and not from structure B.

The NR mass spectra of $CpFeI^{++}$, $CpFeBr^{++}$, and $CpFeCl^{++}$ ions are shown in Figures 1, 2 and 3, respectively. They displayed strong recovery signals, which indicates that stable neutral $CpFeR$ species were generated. The NR mass spectra were similar to the CID mass spectra (cf. Table 1 and Figures 1-3), which showed significant peaks due to $CpFe^+$ and RFe^+ ions. The enhanced intensities of Cp^+ and R^+ ions were due to ionization of the corresponding neutrals generated by collision. It should be noted again that the NR mass spectra showed no ions that have a C—R bond, $C_5H_4R^+$, the presence of which would have indicated the formation of B-type structures.

The CID mass spectra of the recovered $CpFeBr^{++}$ and $CpFeCl^{++}$ ions are listed in Table 1. They are closely similar to those of the precursor $CpFeR^{++}$ ions and to the CID mass spectra of these species metastably generated from $CpFe(CO)R^+$, which shows that no significant changes in the structure of $CpFeR$ species occurred in the neutralization-reionization experiments.

Figure 1. Neutralization-reionization mass spectrum of $CpFeI^{++}$ ions.

In summary, the decomposition characteristics of $CpFeI^{++}$, $CpFeBr^{++}$, and $CpFeCl^{++}$ ions indicate the exclusive existence of isomer A and the formation of their stable neutral counterparts under neutralization-reionization conditions.

$CpFeF^{++}$ Ions

These ions showed richer chemistry than the other halo analogues. In the MI mass spectrum of $CpFeF^{++}$ (Table 1), the most abundant reactions corresponded to the formation of $C_5H_4Fe^+$, $FC_5H_4Fe^+$, and FFe^+ ions. In addition weak peaks due to Cp^+ and Fe^+ ions were present.

The abundance of cyclopentadienyl cations was low relative to the three major decomposition products, but Cp^+ was not observed in the MI mass spectra of the other halogen derivatives. This can be explained easily by a decrease in the ionization energy of XFe^+ radicals in the order $X = F > Cl > Br > I$. The difference between the ionization energy of FFe^+ (unknown, but should exceed that for IFe^+ , 7.8 eV [18]) and Cp^+ (8.41 eV [18]) is probably small enough to allow competition for the positive charge between the products of the $Cp-Fe$ bond cleavage, $[Cp \cdots FeF]^+$.

Collisional excitation of $CpFeF^{++}$ ions (Table 1) resulted in a variety of dissociations that included the

Figure 2. Neutralization-reionization mass spectrum of $CpFe^{79}Br^{++}$ ions.

Figure 3. Neutralization-reionization mass spectrum of $\text{CpFe}^{35}\text{Cl}^{+}$ ions.

decomposition of a coordinated or metal-free cyclopentadienyl ring, which produced $\text{C}_3\text{H}_n\text{FeF}^{+}$ and C_3H_n^{+} ions. No F atom loss was observed in either the MI or CID mass spectra of CpFeF^{+} . Very weak peaks at m/z 84 and 83 that correspond to $\text{C}_5\text{H}_5\text{F}^{+}$ and $\text{C}_5\text{H}_4\text{F}^{+}$ ions were present in the CID mass spectrum, which showed some rearrangement of A ions to structure B. Only trace signals due to these ions were found in the CIDI and NR mass spectra, which indicated very little A ion transformation.

The yield of FFe^{+} , Cp^{+} , and Fe^{+} ions all increased significantly when gas was admitted to the collision cell. Only a small signal due to $\text{C}_5\text{H}_4\text{Fe}^{+}$ was present in the "pure" CID mass spectrum and no detectable increase in the abundance of $\text{FC}_5\text{H}_4\text{Fe}^{+}$ ions was observed. The intensity of the latter remained unchanged when small amounts of the gas were admitted and fell slightly as larger amounts of gas were used.

There are two possible explanations for the above-mentioned observations. One is that all three reactions, for example, Cp^{+} , H^{+} , and HF losses, originated from isomer A. The formation of FFe^{+} (as well as Cp^{+}) is a simple bond cleavage and so is accessible easily upon collisional activation. Reactions that result in $\text{C}_5\text{H}_4\text{FFe}^{+}$ and $\text{C}_5\text{H}_4\text{Fe}^{+}$ ions are, however, rearrangements, which involve intermediate species of unknown structure and which are collisionally insensitive because they can be accessed only at energies close to the dissociation limits. For HF loss, the reaction may involve H atom migration to the fluorine atom followed by a fast loss of HF from the coordination sphere of the metal atom.

The insensitivity of H^{+} elimination and the low sensitivity of HF loss to collisional activation also may result from the isomerization of A ions to another stable isomer, for example, B, prior to dissociation.

To choose between the preceding possibilities, the NR mass spectrum of CpFeF^{+} was recorded; see Figure 4. The CID mass spectra of CpFeF^{+} ions generated from metastable molecular ions of FcCOCF_3 and those that survived neutralization-reionization were examined also. The results are presented in Table 1 together

Figure 4. Neutralization-reionization mass spectrum of CpFeF^{+} ions.

with the MI and CID mass spectra of ion source-generated species.

A comparison of these mass spectra permits one to draw the following conclusions. First, the CID mass spectrum of metastably generated CpFeF^{+} ions was similar to that of ions that survived neutralization-reionization. They also were similar to the CID mass spectrum of ion source-generated CpFeF^{+} . In all these mass spectra the most abundant species were FFe^{+} and $\text{C}_5\text{H}_4\text{Fe}^{+}$ ions, whereas yields of $\text{C}_5\text{H}_4\text{FFe}^{+}$ ions were very small. Metastably generated ions are formed in their ground state or with only a small excess internal energy and so they likely exist as isomerically pure species. In contrast, ions that survive NR are energy rich, but as suggested before, only isomer A has a good chance to survive NR conditions. Thus the close similarity between the m^* -CID and NR-CID mass spectra shows that (1) in both cases ions of A structure were produced and (2) their internal energies were different, but neither regime provided access to structure B. The latter may be accessible only in a very narrow energy range if the energy barrier for $\text{A} \Rightarrow \text{B}$ lies close to A's dissociation limit(s). The observation of both $\text{C}_5\text{H}_4\text{FFe}^{+}$ and $\text{C}_5\text{H}_4\text{Fe}^{+}$ ions in the NR mass spectrum of ion source-generated CpFeF^{+} may indicate the likely coexistence of A and B species prior to their neutralization. The dissociation of a neutral or reionized B isomer could be responsible for a high yield of Fe^{+} ions. However, isomer B cannot play a major role in the chemistry of CpFeF^{+} ions, which mostly exist as structure A.

CpFeO^{+} Ions

Only two peaks were present in the MI mass spectrum of CpFeO^{+} , $\text{C}_4\text{H}_5\text{Fe}^{+}$, and $\text{C}_5\text{H}_5\text{O}^{+}$. The absence of the metal atom in the latter (m/z 81) was shown by their CID mass spectrum, which had no iron-containing fragments.

Neither the CO nor Fe losses are associated readily with the A isomer for CpFeO^{+} ions. It is also unlikely that they originated directly from structure B, which is an oxygen-centred radical (cation). Further isomeriza-

tion to an ion such as C, which involves a 1,2-hydrogen shift in the C_5H_5O ligand, must be proposed to explain the metastable decomposition of $CpFeO^{++}$ ions.

A comparison of the MI mass spectra recorded in the second and third FFR showed that the CO/Fe loss abundance ratio increased by a factor of ~ 5 for ions that have the longer lifetime. Thus for ions of lowest internal energy, rearrangement to species that readily can lose CO competes favourably with Fe loss. CO loss must follow ring opening of a C-type ion and, to compete with metal atom loss, well may involve a simple bond cleavage in the acyclic ligand $CH_2CHCHCHCO$. The ratio of CO/Fe loss was not changed when collision gas was admitted nor did the peaks increase. This is compatible with rearrangement of the initially produced $CpFeO^{++}$ ions to stable isomers, over an energy barrier close to their dissociation limit. If the $CpFeO^{++}$ ions initially have structure A, then rearrangement must take place substantially below the energies for A dissociations. The combined CID-MI mass spectrum (Figure 5a) shows no ions that can be associated easily with structure A except for trace signals that correspond to FeO^{++} and $CpFe^{++}$ ions.

Collisional activation also resulted in a loss of ethyne. $C_3H_3OFe^{++}$ ions generated from collisionally excited $CpFeO^{++}$ precursors were transmitted into the 3FFR and collisionally activated. The resulting CID

mass spectrum exhibited $C_2H_3Fe^{++}$ and did not show either FeO^{++} or $C_3H_3^{++}$ ions, and so $CpFeO^{++}$ ions that decompose by C_2H_2 loss probably did not contain an Fe—O bond.

The NR mass spectrum of $CpFeO^{++}$ (Figure 5b) was dominated by Fe^{++} ions. These species, as indicated by the CIDI mass spectrum, mostly originated from the collisional ionization of neutral metal atoms generated together with $C_5H_5O^{++}$ cations. The latter, as well as the formation of $C_3H_3OFe^{++}$, can be assigned to the decomposition of isomer C or other ions that have hydroxyl-cyclopentadienyl or phenoxylium ligands. However, the observation of $C_4H_5Fe^{++}$ and $C_2H_3Fe^{++}$ ions is explained best by structure C. Abundant $CpFe^{++}$ and FeO^{++} ions that correspond to the dissociation of isomer A were also present.

The yield of recovered $CpFeO^{++}$ ions was too small for their CID mass spectrum to be measured. However, it was possible to record the CID mass spectrum of the species generated from metastable molecular ions of nitroferrocene. This mass spectrum (Figure 5c) was similar to that of ion source-generated ions, with the most abundant species, Fe^{++} , $C_5H_5O^{++}$, and $C_4H_5Fe^{++}$, that correspond to structure C. This observation indicated again that the energy barrier for $A \Rightarrow C$ isomerization must be very low and that isomerically pure A ions were not generated.

The isomer C probably did not survive NR conditions and the weak recovery signal in the NR mass spectrum was assigned to structure A. The internal energy of ions that survive under NR conditions may well be higher than in CID experiments [19]. This may result in new dissociations that were not observed in the CID mass spectra, for example, an important peak due to $CpFe^{++}$ ions was found (Figure 5b).

The present experimental results showed that $CpFeO^{++}$ ions generated from the ionized nitroferrocene ($FcNO_2$) easily rearranged into structure C. To rationalize the experimental observations we proposed a hypothetical energy diagram (Figure 6). In this diagram the B-type ion was considered as an intermediate in the $A \Rightarrow C$ transformation. Activation energies for the decomposition of C were believed to be lower than those for the isomer A. To identify (stable) A species, ions that had higher internal energies had to have been produced under neutralization-reionization conditions.

Figure 5. (a) Combined CID-MI mass spectrum of ion source-generated $CpFeO^{++}$ ions, (b) their NR mass spectrum, and (c) CID mass spectrum of metastably generated ions.

$CpFeOH^{++}$ Ions

The MI mass spectrum of these ions exhibited three major peaks that corresponded to the loss of H_2O , CO, and Cp and minor signals for H, H_2 , and CpOH losses, with relative abundances as shown in Table 1. In addition to the foregoing species, a significant peak at m/z 82 was observed that corresponded to $CpOH^{++}$ ions. These ions also were present in the CIDI mass spectrum of $CpFeOH^{++}$, which indicates that migration of the OH group to the cyclopentadienyl ring occurs

Figure 6. Proposed energy diagram for the isomerization and decomposition of CpFeO^+ ions.

and that at least a fraction of Fe^+ ions was formed from a single-step decomposition of the B-type isomer of CpFeOH^+ ions.

The admission of collision gas had different effects on the peak intensities for the preceding MI reactions. The HOFe^+ ion yield increased steadily as the collision gas was added. Such behavior was consistent with the decomposition of isomer A, which was initially produced from the ferrocene precursors as shown in Scheme I. Collisional excitation of CpFeOH^+ also resulted in Cp^+ and CpFe^+ ions, again indicative of structure A. Only small changes in absolute $\text{HOC}_5\text{H}_4\text{Fe}^+$ ($\text{H}^\cdot$ loss) and $\text{C}_5\text{H}_4\text{Fe}^+$ (H_2O loss) ion yields were observed. These could take place from A ions or isomeric structures. The energies of the corresponding transition states must be relatively low to compete with a simple $\text{Cp}-\text{Fe}$ bond cleavage in the metastable time frame. As with CpFeF^+ ions, weak $\text{H}^\cdot$ and HR (H_2O) losses under collisional excitation can be rationalized by (1) isomerization of structure A prior to these decompositions or (2) by a narrow energy range in which the corresponding transition states (from isomer A) are accessible.

No remarkable changes in $\text{C}_5\text{H}_4\text{OFe}^+$ and $\text{C}_4\text{H}_6\text{Fe}^+$ ion abundances were found when collision gas was admitted. For these reactions too, isomeric $[\text{C}_5, \text{H}_6, \text{O}, \text{Fe}]^+$ structures must be involved. H_2 loss may occur from B and C isomers, but further isomerization to D and/or beyond (Scheme II) is needed for CO loss. The observation of $\text{C}_2\text{H}_3\text{Fe}^+$ ions in the CID mass spectrum provided further evidence for C- and D-type structures. Thus, the insensitivity of these two reactions to collisional activation resulted from the multistep isomerization of structure A (CpFeOH^+).

To assist in the elucidation of mechanisms for CpFeOH^+ ion decomposition, the NR mass spectrum and CID mass spectra of ion source and metastably generated and recovered CpFeOH^+ ions under NR conditions were recorded.

First, the NR mass spectrum displayed a strong recovery signal (Figure 7), which indicated that stable

neutral counterparts of $[\text{C}_5, \text{H}_6, \text{Fe}, \text{O}]^+$ ions were produced in the gas phase. The NR mass spectrum is similar to the "pure" CID of ion source-generated species. Both displayed abundant HOFe^+ ions that, together with the observation of CpFe^+ and Cp^+ ions, was consistent with structure A. Weak signals due to $\text{H}^\cdot$ and H_2O losses were present in the NR mass spectrum, but no $\text{C}_4\text{H}_6\text{Fe}^+$ ions were found.

The CID mass spectrum of $[\text{C}_5, \text{H}_6, \text{Fe}, \text{O}]^+$ ions that survived neutralization-reionization (Table 1) can be presented as a superposition of the MI and CID mass spectra of ion source-generated ions. This result can be rationalized by proposing that the isomer A of CpFeOH^+ ions was generated and that these species possessed a wide range of internal energies that lead to their dissociation and isomerization.

CpFeOH^+ ions that have low internal energy, which were likely isomerically pure species, were produced by the metastable decomposition of FcCOOH^+ . Their CID mass spectrum is shown in Table 1. Ions HOFe^+ and CpFe^+ originated from simple metal-bond cleavage in A-type structure. The observation of a strong signal that corresponded to H_2O loss confirmed that $\text{C}_5\text{H}_4\text{Fe}^+$ ions originated from isomer A. The same conclusion was drawn for CpFeCl^+ and CpFeF^+ ions. No, or only trace, signals for $\text{H}^\cdot$, H_2 and CO losses were observed, which provided a strong indication that rearrangement of A ions must precede these decompositions.

Figure 7. Neutralization-reionization mass spectrum of CpFeOH^+ ions.

In summary, $[C_5, H_6, Fe, O]^{++}$ isomers were identified by their specific decompositions. Ions of structure A ($CpFeOH^{++}$) were generated by metastable decompositions of their ferrocene precursors. This isomer is believed to occupy the global minimum on the potential surface and is responsible for formation of stable neutrals in the NR experiments. Isomerization of A to structure D via isomers B and C may occur in ions that have higher internal energies. However, only A ions that possess a narrow range of internal energy can undergo this isomerization.

$CpFeOMe^{++}$ Ions

The behavior of metastable $CpFeOMe^{++}$ ions was different from that of other oxygen-containing species ($CpFeOH^{++}$ and $CpFeO^{+}$). The MI mass spectrum was dominated by $CpFeCHO^{++}$ and $CpFeH^{++}$ ions that originated from the decomposition of the methoxy group. Both these reactions have been identified earlier in magnetic sector instruments [9, 10, 20, 21]. Isomerization of A ions to structure E is considered to be necessary to produce H_2 and CH_2O (Scheme III). The formation of an isomer that has the CH_2O (formaldehyde) ligand was indicated by the presence of CH_2OFe^{++} ions in the CID and NR mass spectra of $CpFeOMe^{++}$. It is very likely that H atom migration from the metal atom to the cyclopentadienyl ring, preceding the CH_2O loss. The formation of the cyclopentadiene ligand was indicated clearly by the observation of $C_5H_6^{++}$ ions in the combined CID-MI (Figure 8a), CIDI, and NR (Figure 8b) mass spectra.

H_2 loss may occur from structure E or after its further isomerization to G ions. In any case, the coupling of two hydrogen atoms must be a very fast process because the intensity of the metastable peak that corresponds to H_2 loss was as much as 20% of the main beam of $CpFeOMe^{++}$ ions. The barrier for this dissociation likely lies far below the barrier(s) of previous isomerization step(s). This was supported by the observation of an abundant MI mass spectrum for $CpFeOMe^{++}$ ions metastably produced from the molecular ion of $FcCOOMe$. Like the MI mass spectrum of

Figure 8. (a) Combined CID-MI and (b) NR mass spectra of $CpFeOMe^{++}$ ions.

ion source-generated species, this secondary MI mass spectrum was dominated by H_2 loss and showed moderate signals due to CH_2O and MeO losses.

The admission of collision gas to the collision cell affected the MI peaks differently. Yields of $CpFeH^{++}$ and $CpFe^{+}$ ions rose together as the collision gas was added, whereas a significant decrease in H_2 loss abundance was observed. The magnitude of this decrease was very close to the growth in $CpFeH^{++}$ ion abundance. These results demonstrated that collisional activation did not produce any significant yield of ions capable of dissociation by H_2 loss, but instead initiated further decomposition of $CpFeCHO^{++}$ ions by CO loss as shown in Scheme III. The latter reaction has been reported before [9, 20] and also was observed in the present MI and CID experiments.

The MI mass spectrum of $CpFeOMe^{++}$ also showed $CpFe^{+}$ ions, and the CID and NR mass spectra both displayed $CpFe^{+}$ and $MeOFe^{+}$. These two latter species are consistent with the presence of ions that have structure A. Isomer A well may be responsible for the observation of a recovery signal in the NR mass spectrum. However, the yield of surviving ions was low, which may have resulted from significant isomerization of A ions to other isomers that were less stable under NR conditions.

Thus at least a portion of $CpFeOMe^{++}$ ions retained the structure A, but the majority underwent isomerization. Structure E can be proposed as a key intermediate in these transformations to isomers F and G. Structure

Scheme III

G, which originated from migration of the second hydrogen atom to the metal atom, could be responsible for a very fast and irreversible H atom coupling and H₂ loss. The hydride ligand in E ions may migrate to the cyclopentadienyl ring. The $A \Rightarrow E \Rightarrow F$ isomerization is proposed to be reversible and well can be responsible for the H atom mixing that has been observed in C₅H₅FeOCD₃⁺ ions [21].

CpFeH⁺ Ions

Like CpFeOMe⁺, these ions were produced by EI-induced dissociation of methoxycarbonylferrocene molecular ions, where they resulted from C₅H₄CO + CH₂O and C₅H₄CO + H₂ + CO losses. Both reactions have been identified earlier [9, 20, 21] and were confirmed in the present study.

The MI mass spectrum of [C₅, H₆, Fe]⁺ ions was very simple and consisted of two peaks that corresponded to H⁺ and C₅H₆ losses in a ratio of ~ 5:1 (Table 1). CpFe⁺ and Fe⁺ ions were the most abundant species in the CID mass spectrum. Collisional activation also resulted in the decomposition of the hydrocarbon ligand and loss of an Fe atom. The latter reaction gave rise to C₅H₆⁺ ions. These ions together with Fe⁺, dominated the CIDI mass spectrum. Because no HFe⁺ ions were observed, it can be concluded that [C₅, H₆, Fe]⁺ species mostly existed as isomer B. This conclusion was confirmed by the NR mass spectrum, which showed only a trace signal at *m/z* 122. This peak, however, well may correspond to isobaric ¹³CC₄H₅Fe⁺ and C₅H₅⁵⁷Fe⁺ ions, which could not be separated from C₅H₆Fe⁺ in the ion source.

The CID mass spectrum of [C₅, H₆, Fe]⁺ ions produced from metastable CpFeOCH₃⁺ by CH₂O loss was similar to that of the ion source-generated species (Table 1). It should be noted that the CID mass spectra of [C₅, H₆, Fe]⁺ ions that have a C₅H₆ ligand and are formed by the decomposition of C₇H₈Fe⁺ (C₇H₈ = norbornadiene or quadricyclane) [22] or by reaction of Fe(CO)_n⁺ ions with cyclopentadiene [23] are closely similar to those shown in Table 1. Thus, all the experimental data indicate the involvement of structure B for these ions or a mixture of rapidly interconverting structures A and B. The isomerically pure A form of C₅H₆Fe⁺ ions probably cannot be generated from the foregoing precursors because of a low barrier for the $A \Rightarrow B$ isomerization. A similar reaction was observed in ferrocene protonated on the metal atom, which was produced by protonation in an ion cyclotron resonance mass spectrometer and which underwent a reversible rearrangement to CpFe⁺(η⁵-C₅H₆) [24]. The ease of such a transformation in ions that have a coordinative unsaturated metal atom can be even greater [15].

CpFePh⁺ Ions

The MI mass spectrum (Table 1) was dominated by CpPh⁺ ions. Minor fragments corresponded to H⁺, H₂,

and C₂H₂ losses. These species were among the most abundant ions in the CID mass spectrum (Table 1), which also showed intense peaks for C₉H₈⁺ and Fe⁺ ions. No PhFe⁺ and only a trace signal due to CpFe⁺ ions were found, indicating a very high degree of $A \Rightarrow B$ isomerization.

The CIDI mass spectrum of CpFePh⁺ was consistent with the MI and CID mass spectra, which showed peaks due to ionized neutral Fe and CpPh.

The same species as in the CID and CIDI mass spectra were present in the NR mass spectrum of CpFePh⁺, with a very weak recovery signal, abundant Fe⁺ and CpPh⁺ (with accompanying fragmentation), and insignificant CpFe⁺ and PhFe⁺ ions.

The experimental results on CpFePh⁺ ions are consistent with a very low barrier for the Cp and Ph ligand coupling in A-type ions and almost complete transformation of these species to structures B or C.

In an attempt to produce CpFePh⁺ ions of structure A, the species generated in the decomposition of metastable molecular ions of benzoylferrocene (Scheme I) were examined. Their CID mass spectrum (Table 1) showed significant CpFe⁺ and PhFe⁺ ions, which indicated that isomer A was successfully produced. However the presence of abundant signals due to H₂, C₂H₂, and Fe losses showed that even metastably generated CpFePh⁺ ions were not isomerically pure and consisted of a mixture of A and B (or C) structures.

Conclusion

A variety of tandem mass spectrometric methods were used to examine the structure of CpFeR⁺ ions. These ions were generated from the corresponding dicarbonyl complexes (CpFe(CO)₂R) or ferrocene derivatives (FcXR). When newly formed they were believed to have structure A with a Fe—R bond. The experimental data for halogen-containing species were consistent with structure A as the dominant (R = F) or the exclusive species (R = Cl, Br, I).

The behavior of oxygen-containing ions depended on the radical attached to the oxygen atom. The most important decompositions of CpFeOMe⁺ ions involved the isomerization of the methoxy group. The initial step of these rearrangements was hydrogen atom migration to the metal atom. However, some of these species retained their initial A structure.

CpFeO⁺ and CpFeOH⁺ ions easily underwent O or OH migration to the cyclopentadienyl ring, followed by hydrogen rearrangements. As a result of multiple rearrangements, the loss of CO occurred. Isomer A of CpFeOH⁺ ions was stable and easily identified, whereas in the case of CpFeO⁺ only the decomposition of metastable precursors allowed the generation of this isomer.

CpFeH⁺ and CpFePh⁺ ions mostly existed as CpRFe⁺ (B or C) species. Again, isomer A of CpFePh⁺

ions was generated only by metastable decomposition; at higher energies it underwent a facile rearrangement.

Neutralization-reionization experiments greatly assisted the recognition of isomeric species. The presence of abundant recovery ions was assigned to **A** isomers; it was consistent with the other experimental data. The NR mass spectra of $CpFeR^{+}$ ions also contained structure-indicative fragment ions. These species arose from simple $Cp-Fe$ and $Fe-R$ bond cleavages that required high internal energy, which could less easily be accessed by ions in CID experiments.

The observation of recovery signals demonstrated that stable neutral counterparts of $CpFeR^{+}$ ions ($R =$ halogen, O, OH), were generated in the gas phase. These coordinatively unsaturated species possessed no solvent molecules or other stabilizing ligands at the metal atom—adducts whose presence is necessary for $CpFeCl$, $CpFeBr$, and $CpFeI$ to be stable in the condensed phase. Their analogues, which have O, F, or OH as a ligand (not a counterion) at the metal atom connected to the π -cyclopentadienyl ring, have not been reported and were produced in the present work for the first time. It is apparent that many other species of the type $CpFeR$ can be generated in neutralization-reionization experiments, which necessitates the production of their positively or negatively charged analogues in the gas phase. As with many other transition metal complexes that contain *even-electron molecule(s)* as a ligand, ionized substituted cyclopentadiene iron derivatives hardly survive NR conditions and some special effort should be made to observe their recovery signals and to confirm their structure.

References

1. See, for example, Jutzi, P. *Adv. Organomet. Chem.* **1986**, 26, 217.
2. Zagorevskii, D. V.; Holmes, J. L. *Mass Spectrom. Rev.* **1994**, 13, 133.
3. Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E.; Terlouw, J. K. *Org. Mass Spectrom.* **1984**, 19, 442.
4. Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1956**, 3030.
5. Perevalova, E. G.; Nikitina, T. V. In *Organometallic Reactions*; Becker, E. I.; Tsutsui, M., Eds.; Wiley-Interscience: New York, 1971, Vol. 4, p 163.
6. Traeger, J. C.; Mommers, A. A. *Org. Mass Spectrom.* **1987**, 22, 592.
7. Schumacher, E.; Taubenest, R. *Helv. Chim. Acta* **1966**, 49, 1447.
8. Bruce, M. I. *Int. J. Mass Spectrom. Ion Phys.* **1968**, 1, 141.
9. Mandelbaum, A.; Cais, M. *Tetrahedron Lett.* **1964**, 3847.
10. Zagorevskii, D. V. Ph.D. Thesis, Institute of Organoelement Compounds, Moscow, 1981.
11. Egger, H. *Monatsch. Chem.* **1966**, 97, 602.
12. Mechtler, H.; Schlögl, K. *Monatsch. Chem.* **1966**, 97, 754.
13. Clifford, A. F.; Mukherjee, G. *Inorg. Synth.* **1966**, 8, 185.
14. Clancy, D. J.; Spilners, J. J. *Anal. Chem.* **1962**, 34, 1839.
15. Nekrasov, Yu. S.; Zagorevskii, D. V. *Applications of Mass Spectrometry to Organic Stereochemistry*; Splitter, J. S.; Tureček, F., Eds.; VCH: New York, 1994; Chap. 22.
16. Schröder, D.; Fiedler, A.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1994**, 134, 239.
17. Schröder, D.; Sulzle, D.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, 110, 145.
18. Lias, S. C.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Ref. Data* **1978**, 17, Suppl. 1.
19. Beranová, Š.; Wesdemiotis, C. *J. Am. Soc. Mass Spectrom.* **1994**, 5, 1093.
20. Roberts, D. T.; Little, W. F.; Bursey, M. M. *J. Am. Chem. Soc.* **1967**, 89, 6156.
21. King, R. B. *J. Am. Chem. Soc.* **1968**, 90, 1417.
22. MacMillan, D. K.; Hayes, R. N.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1992**, 114, 7801.
23. Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, 106, 4310.
24. Hop, C. E. C. A.; McMahon, T. B. *J. Am. Soc. Mass Spectrom.* **1994**, 5, 274.