was removed under reduced pressure, the residue was extracted with *n*-pentane (2 × 25 ml) and filtered, and the pentane was removed under reduced pressure to give $D_2Os_3(CO)_{12}$ as a pale yellow crystalline solid (0.086 g, 63%). The product was purified by sublimation (70 °C (0.01 mm)); mp 92–97 °C. Anal. Calcd for $C_{12}D_2O_{12}Os_3$: C, 15.83; D, 0.44; O, 21.09; mol wt 911.846. Found: C, 15.93; D, 0.83; O, 21.24; mol wt (mass spectrometrically) 911.843.

Dideuteriooctacarbonyldiosmium. $Os_2Cl_2(CO)_8$ (0.14 g) as a suspension in CH_3OD (8 ml) was refluxed under nitrogen for 10 min with zinc dust (0.23 g) and CH_3COOD (0.05 g). The solvent was removed under reduced pressure, the residue was extracted with pentane (2 × 30 ml) and filtered, and the pentane was removed under reduced pressure leaving the product as a pale yellow oil (0.06 g, 48%). The product was purified by condensation onto a water-cooled probe (30 °C (0.01 mm)) and identified mass spectrometrically (mol wt: calcd for $C_8D_2O_8Os_2$, 609.908; found, 609.909).

Reaction of $Os_3(CO)_{12}$ with Hydrogen. A 200-ml autoclave was charged with triosmium dodecacarbonyl (0.24 g), *n*-heptane (15 ml), and hydrogen (33 atm) and heated with magnetic stirring at 95 °C for 67 h. After the bomb was cooled and the gases were vented, the ir spectrum of the reaction solution showed the main product to be $H_2Os_3(CO)_{10}$ together with $H_2Os_2(CO)_8$, $H_2Os(CO)_4$, and unreacted $Os_3(CO)_{12}$. The solvent and $H_2Os(CO)_4$ were removed under reduced pressure and the residue was recrystallized several times from pentane to give a low yield of red crystals whose ir spectrum was identical with that of an authentic sample of $H_2Os_3(CO)_{10}$.[5,6] A molecular ion was observed in the mass spectrum.

Registry No. $H_2Os_2(CO)_8$, 25685-05-6; $H_2Os_3(CO)_{12}$, 60645-64-9; $H_2Os_3(CO)_{10}$, 11063-23-3; $H_2Os_4(CO)_{16}$, 60645-65-0; $H_2Os(CO)_4$, 18972-42-4; $D_2Os_2(CO)_8$, 60645-66-1; $D_2Os_3(CO)_{12}$, 60645-67-2; OsO_4, 20816-12-0; $Os_3Br_2(CO)_{12}$, 21773-71-7; $Os_2Cl_2(CO)_8$, 25685-06-7; $Os_3(CO)_{12}$, 15696-40-9.

Supplementary Material Available: Tables A and B and Figure A, all showing mass spectra (4 pages). Ordering information is given on any current masthead page.

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Mass Spectra of Organometallic Compounds. 4. Electron-Impact Study of Some Cyclopentadienylmetal Carbonyl Dimers

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The mass spectra of the cyclopentadienylmetal carbonyl dimers $[QCr(CO)_2]_2$ ($Q = C_5H_5$, C_5Me_5), $[C_5H_5Fe(CO)_2]_2$, and $[C_5H_5Ni(CO)]_2$ have been examined and the appearance potentials of most of the metal-containing fragment ions, those with all ligands, determined. The primary fragmentations in the mass spectra of these complexes have been assigned and compared.

Introduction

Despite the large volume of mass spectral data on organometallic compounds,[1] relatively little has so far been done to confirm proposed fragmentation schemes. In general, metastable transitions, few of which are normally found in most mass spectra of organometallic compounds, do provide positive proof of specific fragmentations. However, these specific fragmentations are not necessarily the main sources

of ions. Useful information for the assignment of fragmentations can be obtained from appearance potential data. Generally, under electron-impact conditions most organometallic ions exhibit one detectable appearance potential and this probably suggests the existence of a single primary precursor for each of the ions. Predominant processes by which fragment ions are produced will henceforth be referred to as primary fragmentations. In a primary fragmentation sequence,

Table I. Intensities (I) (at 80 eV) and Appearance Potentials (AP) of the Metal-Containing Ions in the Mass Spectra of $Q_2Cr_2(CO)_4$ [1, $Q = C_5Me_5$ and Cp]

	$Q = C_5Me_5$			$Q = Cp$		
	m/e	I^a	AP,^{a} eV	m/e	I^b	AP,^{c} eV
			Monopositive Ions			
$[Q_2Cr_2(CO)_4]^+$	486	0.3	5.89 ± 0.11	346	0.6	6.74 ± 0.06
$[Q_2Cr_2(CO)_3]^+$	458	34.4	7.08 ± 0.02	318	17.5	7.54 ± 0.04
$[Q_2Cr_2(CO)_2]^+$	430	0.6	9.64 ± 0.04	290	4.7	8.90 ± 0.02
$[Q_2Cr_2(CO)]^+$	402	8.5	10.52 ± 0.12	262	2.6	9.28 ± 0.03
$[Q_2Cr_2]^+$	374	100.0	12.32 ± 0.15	234	8.4	10.53 ± 0.03
$[Q_2Cr]^+$	322	71.9	13.74 ± 0.05	182	100.0	12.58 ± 0.02
$[QCr(CO)_3]^+$	271	4.6	7.05 ± 0.02			
$[QCr(CO)_2]^+$	243	5.2	7.37 ± 0.06	173	10.7	7.62 ± 0.10
$[QCr(CO)]^+$	215	7.0^d	8.24 ± 0.04	145	13.9	9.17 ± 0.04
$[QCr]^+$	187	63.4	11.4 ± 0.08	117	66.7	12.53 ± 0.10
$[Cr]^+$	52	30.0	18.12 ± 0.15	52	35.6	14.97 ± 0.07
			Dipositive Ions			
$[Q_2Cr_2(CO)_3]^{2+}$	229	1.4	19.21 ± 0.06			
$[Q_2Cr_2(CO)_2]^{2+}$	215	7.0^d	19.80 ± 0.29			
$[Q_2Cr_2(CO)]^{2+}$	201	1.0	20.53 ± 0.19			
$[QCr(CO)]^{2+}$	107.5	0.5	20.92 ± 0.03	72.5	0.8	
$[QCr]^{2+}$	93.5	2.0	22.22 ± 0.10	58.5	1.1	

	$Q = C_5Me_5$			$Q = Cp$	
Other ions	m/e	I^a	Other ions	m/e	I^b
$[C_{19}H_{27}Cr]^+$	307	2.0	$[C_5H_5Cr]^+$	115	3.5
$[C_{10}H_{13}Cr]^+$	185	19.0	$[C_3H_3Cr]^+$	91	2.0
$[C_9H_{12}Cr]^+$	172	5.0	$[C_3H_2Cr]^+$	90	3.6
$[C_9H_{11}Cr]^+$	171	1.8	$[C_3HCr]^+$	89	0.7
$[C_8H_{11}Cr]^+$	159	2.0	$[C_2H_2Cr]^+$	78	0.5
$[C_8H_9Cr]^+$	157	1.0	$[C_2H Cr]^+$	77	1.5

^{a} SHT and ICT were both kept at 200 ± 2 °C. ^{b} SHT, 130 ± 2 °C; ICT, 200 ± 2 °C. ^{c} SHT, 90 ± 2 °C; ICT, 100 ± 2 °C. ^{d} Sum of the intensities of the mono- and dipositive ions with m/e 215.

subsequent ions are expected to exhibit higher appearance potentials due to the endothermicity of the bond-breaking processes involved. Moreover, the energetics of primary fragmentations should provide estimates of ionic bond dissociation energies. Bond energies determined by this technique may not be accurate in an absolute sense because of indeterminate errors due to kinetic and excitation energies of the participant ions. Nonetheless, in analogous complexes whose mass spectra consist of similar fragmentations it may be reasonable to expect these indeterminate errors to be about equal. Under these circumstances, the relative scale of ionic bond dissociation energies should be meaningful and reflect the relative order of metal-to-ligand bond strengths in the parent molecules. In view of the foregoing, it is apparent that a better understanding of fragmentation processes can be achieved by examining the appearance potential of ions. This has been attempted in the case of several related cyclopentadienylmetal carbonyl dimers of the first-row transition elements.

The mass spectra of several binuclear complexes of the type $[QM(CO)_n]_2$ ($Q = C_5H_5$, M = Cr, n = 3;[2] $Q = C_5H_5$, M = Fe, n = 2;[3,4] Q = C_5H_5, M = Ni, n = 1;[4] Q = C_5Me_5, M = Cr, n = 2[5]) have already been reported; however, so far, no attempt has been made to confirm their fragmentation schemes. Except for the spectrum of the chromium complex $Q = C_5H_5$, M = Cr, n = 3, which shows the conspicuous absence of bimetallic ions,[2] the spectra of the remaining complexes exhibit similar mono- and bimetallic ions. In an attempt to identify the primary fragmentations in the mass spectra of these complexes as well as those of the chromium complex $Q = C_5H_5$, M = Cr, n = 2,[6] the appearance potential of most of the metal-containing ions, those with all ligands, have been determined and analyzed. The energetics of certain fragmentation processes, obtained from relevant appearance potential data, have been examined in order to ascertain possible effects due to the π ligand and/or the multiplicity of

the M–M bond on the modes of fragmentation.

Experimental Section

The dimers $Q_2Cr_2(CO)_4$ [1; Q = Cp[6] (henceforth, short for η^5-cyclopentadienyl) and C_5Me_5[5]], $Cp_2Fe_2(CO)_4$ (2),[7] and $Cp_2Ni_2(CO)_2$ (3)[8] were prepared and purified according to published procedures. The mass spectra of these compounds were measured at 80 eV on a Hitachi RMU-7E mass spectrometer which had been modified with a Keithley 427 current amplifier. The samples were introduced directly into the ionization chamber of the mass spectrometer under a low pressure of $\sim 10^{-6}$ Torr. The conditions [sample heater temperature (SHT) and ionization chamber temperature (ICT)] used in obtaining the spectra are specified in Tables I–III which contain the following information concerning metal-containing ions: (1) intensities (I) of ions, those containing the most abundant isotopes of the element involved, given relative to an arbitrary value of 100.0 chosen for the base peak and that of the most intense ion in each spectrum; (2) appearance potentials (AP) of ions, determined by a modified Honig method[9] according to the procedure of Lossing, Tickner, and Bryce[10] using benzene (i = 9.44 eV)[11] as a calibrant; (3) relative ion currents (RIC) (Tables II and III, only), calculated from the intensity of individual ions (I_i) and the sum of intensities ($\sum I_i$) of the metal-containing ions according to ($I_i \times 100$)/$\sum I_i$.

The complexes under study (1–3) were found to exhibit sufficient thermal stability under the specified conditions utilized in obtaining their mass spectra. Metastable ions found in the spectra of the chromium complexes 1, Q = Cp and C_5Me_5, are listed in Table IV.

The appearance potential of each ion was measured several times independently and the precision of the mean result is indicated by the quoted standard deviation (Tables I–III). The accuracy of the results is probably an order of magnitude lower than the indicated precision terms, although this could not be determined unambiguously.

Results and Discussion

In the mass spectrum (80 eV) of 1, Q = C_5Me_5, two primary fragmentation sequences are initiated from the molecular ion (MI). The first involves a four-step, unimolecular carbonyl dissociation sequence via the bimetallic ions $[Q_2Cr_2(CO)_{4-n}]^+$ (n = 0–4) and the rearrangement of the

Table II. Intensities (I) (at 80 eV), Appearance Potentials (AP), and Relative Ion Currents (at 80 eV) of the Major Metal-Containing Ions in the Mass Spectrum of $Cp_2Fe_2(CO)_4$ (2)

m/e	Ion	I^a	$AP,^a$ eV	Relative current,^{b} %, at SHT						
				120 °C	130 °C	140 °C	150 °C	160 °C	170 °C	180 °C
354	$[Cp_2Fe_2(CO)_4]^+$	18.8	6.82 ± 0.02	7.6	5.5	5.5	4.9	4.5	4.4	3.9
326	$[Cp_2Fe_2(CO)_3]^+$	12.5	7.62 ± 0.02	4.9	3.7	3.5	3.3	3.1	2.9	2.6
298	$[Cp_2Fe_2(CO)_2]^+$	20.5	8.99 ± 0.04	7.9	6.3	6.0	5.6	4.7	4.7	4.4
270	$[Cp_2Fe_2(CO)]^+$	7.9	9.71 ± 0.02	2.8	2.2	2.2	2.1	1.9	1.9	1.7
242	$[Cp_2Fe_2]^+$	50.4	11.96 ± 0.04	17.3	14.6	14.3	13.2	12.4	12.2	11.6
186	$[Cp_2Fe]^+$	100.0	7.60 ± 0.04	27.4	27.2	26.2	26.2	25.3	25.2	24.5
177	$[CpFe(CO)_2]^+$	17.3	7.86 ± 0.05	3.1	4.3	4.3	4.5	4.5	4.5	4.9
149	$[CpFe(CO)]^+$	19.7		4.0	4.7	5.2	5.1	5.4	5.4	5.4
121	$[CpFe]^+$	93.7	10.43 ± 0.02	17.3	23.1	22.9	24.5	26.0	26.1	27.6
112	$[Fe_2]^+$	3.9		0.8	1.1	1.0	1.0	1.1	1.1	1.1
56	$[Fe]^+$	37.4		6.7	7.2	8.6	7.8	10.8	11.5	12.3

^{a} SHT, 150 ± 2 °C; ICT, 200 ± 2 °C. ^{b} ICT, 200 ± 2 °C.

Table III. Intensities (I) (at 80 eV), Appearance Potentials (AP), and Relative Ion Currents (at 80 eV) of the Major Metal-Containing Ions in the Mass Spectrum of $Cp_2Ni_2(CO)$ (3)

m/e	Ion	I^a	$AP,^a$ eV	Relative current,^{b} %, at SHT						
				80 °C	90 °C	100 °C	110 °C	120 °C	130 °C	140 °C
302	$[Cp_2Ni_2(CO)_2]^+$	18.7	7.05 ± 0.02	7.1	7.1	6.5	6.8	6.4	6.3	5.9
274	$[Cp_2Ni_2(CO)]^+$	5.0	7.87 ± 0.05	1.8	1.6	1.6	1.5	1.5	1.5	1.6
246	$[Cp_2Ni_2]^+$	75.0	9.05 ± 0.02	30.3	29.1	28.9	29.0	28.9	28.4	27.1
188	$[Cp_2Ni]^+$	100.0	7.33 ± 0.02	39.2	39.9	40.0	39.5	39.2	39.2	39.4
123	$[CpNi]^+$	40.6	13.66 ± 0.03	16.0	17.1	17.5	17.5	17.5	17.9	18.8
58	$[Ni]^+$	14.82		5.0	5.1	5.3	5.6	6.4	6.7	7.2

^{a} SHT, 90 ± 2 °C; ICT, 50 ± 2 °C. ^{b} ICT, 50 ± 2 °C.

Scheme I. Primary Fragmentation in the Mass Spectra (at 80 eV) of $Q_2Cr_2(CO)_4$ [1, Q = C_5Me_5 and Cp]
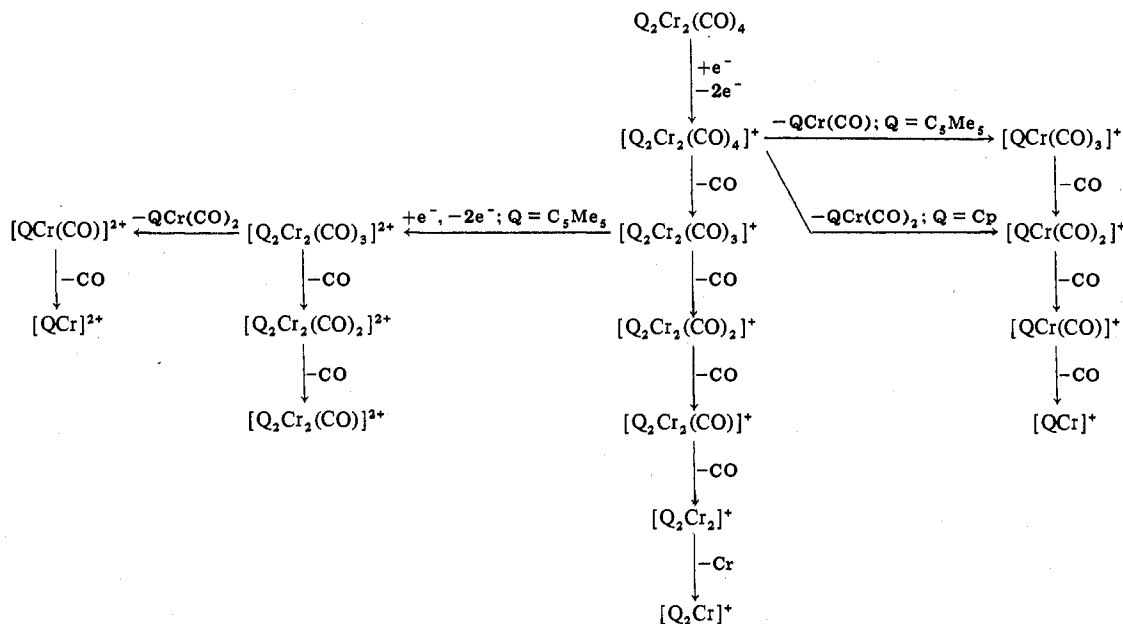
carbonyl-free ion (n = 4) to permethylated chromocenium by a process involving C_5Me_5 transfer and chromium atom elimination. In the second sequence, the MI is cleaved asymmetrically to afford $[QCr(CO)_3]^+$ which then decarbonylates to $[QCr]^+$ via a normal three-step process. A noteworthy feature in the mass spectrum of this complex is the presence of significant amounts of various dipositive ions. The origin of these ions is presumed from $[Q_2Cr_2(CO)_3]^+$ rather than the MI, since the ion current of the former is considerably greater (over 100-fold). The detection of only one AP at m/e 243 due to $[QCr(CO)_2]^+$ (7.37 eV) might suggest against the presence of the doubly charged MI in the mass spectrum of this complex. The stepwise decarbonylation of $[Q_2Cr_2(CO)_3]^{2+}$ is supported by the presence of the appropriate metastable ions (Table IV) and its cleavage to

$[QCr(CO)]^{2+}$ might be suggested by the absence of $[QCr(CO)_2]^{2+}$ and the low probability of ionizing $[QCr(CO)]^+$, whose ion current in the spectrum is relatively low. The fragmentations described above, given in Scheme I, are compatible with the appearance potentials of the ions involved; hence, they probably represent primary pathways. Another feature of interest in this spectrum is the simultaneous loss of two carbonyl groups from $[Q_2Cr_2(CO)_3]^+$, a process which is supported by the presence of an appropriate metastable ion (Table IV). This process has been ruled to be secondary since it requires higher energy than that needed for the competitive fragmentation by which $[Q_2Cr_2(CO)_2]^+$ is formed. Apart from fragmentations involving metal-containing ions with all ligands, the disintegration of the coordinated C_5Me_5 ligand is also noteworthy. This appears to be initiated by the de-

Table IV. Metastable Ions (M*) Found in the Mass Spectra of $Q_2Cr_2(CO)_4$ [1, $Q = C_5Me_5$ and Cp]

	M*(found)^a	
Process	$Q = C_5Me_5$	$Q = Cp$
$[Q_2Cr_2(CO)_3]^+ \rightarrow [Q_2Cr_2(CO)_2]^+ + CO$	403.7 m	264.5 s
$[Q_2Cr_2(CO)_2]^+ \rightarrow [Q_2Cr_2(CO)]^+ + CO$	375.8 m	236.7 s
$[Q_2Cr_2(CO)]^+ \rightarrow [Q_2Cr_2]^+ + CO$	347.9 s	209.0 vw
$[Q_2Cr_2]^+ \rightarrow [Q_2Cr]^+ + Cr$	277.2 vw	141.6 s
$[(Me_5C_5)_2Cr_2(CO)_3]^+ \rightarrow [(Me_5C_5)_2Cr_2(CO)]^+$ $+ 2CO$	352.9 s	
$[(Me_5C_5)_2Cr]^+ \rightarrow [Me_5C_5CrC_5Me_4]^+ + Me$	292.1 w	
$[(Me_5C_5)_2Cr_2(CO)_3]^{2+}$ $\rightarrow [(Me_5C_5)_2Cr_2(CO)_2]^{2+} + CO$	201.9 vw	
$[(Me_5C_5)_2Cr_2(CO)_2]^{2+} \rightarrow [(Me_5C_5)_2Cr_2(CO)]^{2+}$ $+ CO$	187.9 w	
$[(Me_5C_5)Cr]^+ \rightarrow [(C_{10}H_{13})Cr]^+ + 2H$	183.0 m	

^{a} Relative intensities: m, medium; s, strong; vw, very weak; w, weak.

Scheme II. Primary Fragmentations in the Mass Spectra (at 80 eV) of $Cp_2M_2(CO)_{2n}$ [2, M = Fe, $n = 2$; 3, M = Ni, $n = 1$]

methylation of $[Q_2Cr]^+$ ($\rightarrow[C_{19}H_{27}Cr]^+$; M*, 292.1) and $[QCr]^+$ ($\rightarrow[C_9H_{12}Cr]^+$) and the dehydrogenation of $[QCr]^+$ ($\rightarrow[C_{10}H_{13}Cr]^+$). The formation of the other metal-containing ions with partial ligand can be explained in terms of the consecutive demethylation of $[C_{10}H_{13}Cr]^+$ ($\rightarrow[C_9H_{11}Cr]^+ \rightarrow [C_8H_9Cr]^+$) and the CH elimination from $[C_9H_{12}Cr]^+$ ($\rightarrow[C_8H_{11}Cr]^+$).

On the outset, the fragmentation of **1**, Q = Cp, under electron-impact (80 eV) conditions appears to resemble that of **1**, $Q = C_5Me_5$ (Scheme I). The main differences between the two spectra, other than those arising from the rupture of the coordinated ligand Q, are as follows: (1) the MI in the Q = Cp derivative undergoes symmetric cleavage to $[CpCr(CO)_2]^+$ in contrast with the asymmetric cleavage encountered in the instance of the $Q = C_5Me_5$ analogue; (2) the formation of dipositive ions appears to be greatly favored when $Q = C_5Me_5$; (3) evidence in support of the simultaneous loss of two carbonyl groups from $[Cp_2Cr_2(CO)_3]^+$ could not be found, whereas a similar process in the instance of Q = C_5Me_5 was verified by the presence of an appropriate metastable ion. The rupture of the coordinated cyclopentadienyl ligand appears to originate from $[CpCr]^+$ and involves processes such as dehydrogenation ($\rightarrow[C_5H_3Cr]^+$) and deacetylenation ($\rightarrow[C_3H_3Cr]^+$). The other metal-containing ions with partial cyclopentadienyl ligand probably originate from $[C_3H_3Cr]^+$ by processes involving consecutive dehydrogenation ($\rightarrow[C_3H_2Cr]^+ \rightarrow [C_3HCr]^+$) and CH elimination ($\rightarrow[C_2H_2Cr]^+$) followed by dehydrogenation ($\rightarrow[C_2HCr]^+$).

Apart from the chromium complexes (**1**, Q = Cp and C_5Me_5), the fragmentations of cyclopentadienylmetal carbonyl dimers $Cp_2Fe_2(CO)_4$ (**2**) and $Cp_2Ni_2(CO)_2$ (**3**) have also been examined in detail during the course of this investigation. In order to ascertain the primary fragmentations in the mass spectra of these complexes, the appearance potentials of most of the metal-containing ions, those with all ligands, have been determined and analyzed. The mass spectral data of **2** (Table II) and **3** (Table III) favorably support the primary fragmentations given in Scheme II. The ions $[CpFe(CO)_3]^+$ and $[CpNi(CO)]^+$, which give rise to low-intensity peaks in spectra taken at 20 eV,[4] are absent from the spectra run at 80 eV and therefore have not been included in Scheme II. The cleavage of the MI in **3** is of minor significance compared with the same process in **2** and this is evident, inter alia, from the considerably higher AP of $[CpNi]^+$ (13.66 eV) than that of $[CpFe]^+$ (10.43 eV). Possible primary precursors of the latter ion are $[CpFe(CO)]^+$, whose AP could not be determined, and $[Cp_2Fe]^+$ (7.60 eV). The formation of $[CpFe]^+$ from $[Cp_2Fe_2]^+$ (11.96 eV) has been ruled out in view of the
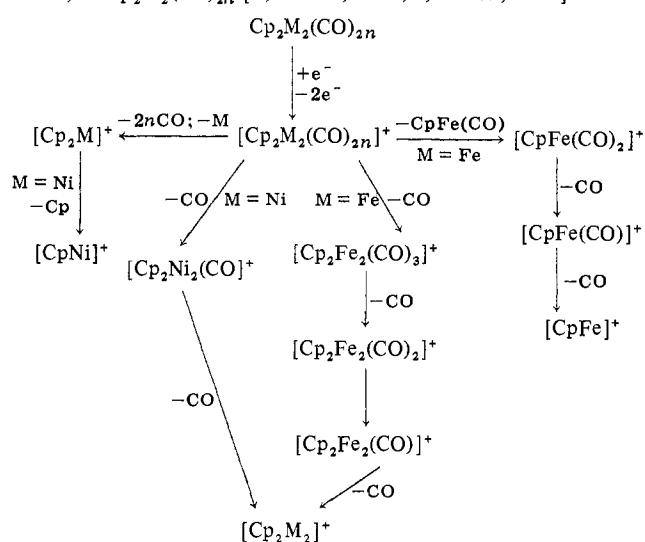
significantly higher AP of the latter ion. Among the two alternative primary precursors of $[CpFe]^+$, the ferrocenium ion can be ruled out based on the comparison between the energetics of the process $[Cp_2Fe]^+ \rightarrow [CpFe]^+ + Cp$ in the spectra of **2** and ferrocene. In the instance of ferrocene such a process has been shown to involve the energetics of 6–7 eV,[12] and this contrasts with the value of 2.8 eV suggested for the same process in **2**, based on the appropriate AP data given in Table II. The foregoing would therefore support the view that the predominant source of $[CpFe]^+$ in the mass spectrum of **2** is the low-energy pathway involving the consecutive decarbonylation of $[CpFe(CO)_2]^+$. In contrast with the iron dimer, either $[Cp_2Ni]^+$ (7.33 eV) or $[Cp_2Ni_2]^+$ (9.05 eV) can be conceived as viable primary precursors of $[CpNi]^+$; the former precursor is favored since the energetics of $[Cp_2Ni]^+$ $\rightarrow [CpNi]^+ + Cp$ in **3** (6.33 eV) is similar to that found for the analogous process in the mass spectrum of nickelocene (5.4 eV).[12]
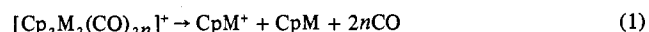
Decarbonylations via bimetallic ions in the mass spectra of **2** and **3** are consistent with the increase in the AP of subsequent ions in the sequences; this issue will be dealt with in further detail elsewhere in this paper. At present, it should be of interest to examine the formation of the metallocenium ion $[Cp_2M]^+$ (M = Fe, Ni). In contrast with the chromium complexes **1**, Q = Cp and C_5Me_5, the primary source of $[Cp_2M]^+$ (M = Fe, Ni) in the mass spectra of **2** and **3** does not appear to be the bimetallic ion $[Cp_2M_2]^+$, although metastable peaks in support of such a process have been found in both spectra.[4] The respective metallocenes in the mass spectra of **2** and **3** are formed with a potential next lowest from that of the MI. These potentials are considerably lower than those of the bimetallic ions $[Cp_2M_2]^+$ (M = Fe, Ni). In view of the foregoing, the primary source of these metallocenium ions could presumably be from either the MI or Cp_2M (M = Fe, Ni); the latter might be produced thermally from the parent molecule prior to ionization. In order to ascertain the latter possibility, the relative ion currents of $[Cp_2Fe]^+$ (Table II) and $[Cp_2Ni]^+$ (Table III) have been measured as a function of the sample heater temperature. The thermal productions of Cp_2M should have resulted with substantial increase in the relative ion current of $[Cp_2M]^+$ (M = Fe, Ni) at higher sample heater temperature; however, this evidently has not been observed. The data furnished in Tables II and III reveal rather small variations in the relative ion currents of these ions which are similar to those found for the other metal-containing ions in both spectra. Further evidence in

Table V. Specific and Mean Metal-to-Carbonyl Ionic Bond Dissociation Energies for the Decarbonylation of Bimetallic Ions in **1** (Q = C_5Me_5 and Cp), **2**, and **3**

		Ionic bond dissociation			
		Energy, eV			
Assumed process	Type[a]	1, Q = C_5Me_5	1, Q = Cp	2 (Q = Cp)	3 (Q = Cp)
$[Q_2M_2(CO)_4]^+ \rightarrow [Q_2M_2(CO)_3]^+ + CO$	$D(M^+-CO)^1$	1.19	0.8	0.8	
$[Q_2M_2(CO)_3]^+ \rightarrow [Q_2M_2(CO)_2]^+ + CO$	$D(M^+-CO)^2$	2.56	1.36	1.37	
$[Q_2M_2(CO)_2]^+ \rightarrow [Q_2M_2(CO)]^+ + CO$	$D(M^+-CO)^3$	0.88	0.38	0.72	
$[Q_2M_2(CO)]^+ \rightarrow [Q_2M_2]^+ + CO$	$D(M^+-CO)^4$	1.80	1.25	2.25	
$^1/_4[Q_2M_2(CO)_4]^+ \rightarrow {}^1/_4[Q_2M_2]^+ + CO$	$\bar{D}(M^+-CO)$	1.61	0.95	1.28	
$[Cp_2Ni_2(CO)_2]^+ \rightarrow [Cp_2Ni_2(CO)]^+ + CO$	$D(Ni^+-CO)^1$				0.82
$[Cp_2Ni_2(CO)]^+ \rightarrow [Cp_2Ni_2]^+ + CO$	$D(Ni^+-CO)^2$				1.18
$^1/_2[Cp_2Ni_2(CO)_2]^+ \rightarrow {}^1/_2[Cp_2Ni_2]^+ + CO$	$\bar{D}(Ni^+-CO)$				1.00

[a] The superscripts indicate the number of steps the carbonyl dissociation is removed from the molecular ion.

support of the above conclusion comes from the somewhat lower ionization potentials of the parent metallocenes Cp_2M (M = Fe, Ni)[13] as compared with the AP of the respective ions $[Cp_2M]^+$ (M = Fe, Ni) in the mass spectra of **2** and **3**. The formation of metallocenium from the MI, presumed to take place in the mass spectra of **2** and **3**, can be rationalized in terms of a simultaneous cyclopentadienyl-transfer, decarbonylation, and metal-elimination process. Thermodynamically, such a process can be broken in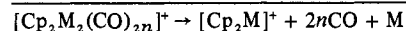to three individual steps (eq 1-3) whose heat of reactions (ΔH) might be expressed in terms of bond dissociation energies. The individual

$$[Cp_2M_2(CO)_{2n}]^+ \rightarrow CpM^+ + CpM + 2nCO \quad (1)$$

$$\Delta H_1 \approx D(M^+-M) + 2n\bar{D}(M^+-CO)$$

$$CpM \rightarrow Cp + M \quad (2)$$

$$\Delta H_2 \approx D(M-Cp)$$

$$[CpM]^+ + Cp \rightarrow [Cp_2M]^+ \quad (3)$$

$$\Delta H_3 \approx -D(CpM^+-Cp)$$

$$[Cp_2M_2(CO)_{2n}]^+ \rightarrow [Cp_2M]^+ + 2nCO + M$$

$$\Delta H \approx D(M^+-M) + 2n\bar{D}(M^+-CO) + D(M-Cp) - D(CpM^+-Cp)$$

pressed in terms of bond dissociation energies. The individual steps are presumed endothermic or exothermic depending on whether bonds are being cleaved or formed, respectively. In order to solve for ΔH, the respective bond dissociation energies need to be known first. These bond energies can be estimated in the instance of the iron complex **2** in the following manner. The terms $2n\bar{D}(Fe^+-CO)$ and $D(Fe^+-Fe)$ can be estimated from the appropriate appearance potentials data of **2** (Table II) as 5.14 and 1.04 eV, respectively. The value of $D(CpFe^+-Cp)$, determined from mass spectral data of ferrocene,[12] is 6.60 eV while that of neutral $D(Fe-Cp)$, although not known, should differ by only little from the ionic term $D(Fe^+-Cp) = 0.60$ eV for ferrocene.[12] On the basis of the above bond dissociation energies, the heat of reaction for the overall process (ΔH) might be estimated at about 0.18 eV; this result is consistent with the low energetics of 0.78 eV determined for the same presumed process from the IP of **2** and the AP of the ferrocenium in the mass spectrum of this complex. The presence of nickelocenium in the mass spectrum of **3** could conceivably be explained in analogous terms. In contrast, the different mode of formation of chromocenium in the mass spectra of **1**, Q = Cp and C_5Me_5, could perhaps be attributed to the presence of a strong Cr–Cr bond of a triple multiplicity in these complexes. An increase in $D(M^+-M)$ should decrease the probability of the simultaneous process by which chromocenium might be formed from the MI. At the outset, this explanation appears to be inconsistent with the symmetric cleavage energies of 0.88 eV (**1**, Q = Cp) and 1.04 eV (**2**). However, this apparent discrepancy might reflect the constraint geometry of **1**, Q = Cp, which probably arises from repulsive forces of steric origin due to the close proximity of

the halves of the MI as in the instance of **1**, Q = C_5Me_5, whose crystal structure has been resolved.[14] Such repulsive forces are expected to be considerably smaller in **2** and **3** where the M–M bonds are significantly longer than those in the chromium complexes. Therefore, in the instance of **2**, the cleavage energy of the MI should relate more intimately to the intrinsic strength of the M–M bond than in the case of **1**, Q = Cp.

The specific and mean metal-to-carbonyl ionic bond dissociation energies for the decarbonylation processes via bimetallic ions in **1**, Q = Cp and C_5Me_5, **2**, and **3** have been computed from the relevant AP data (Tables I–III) and are listed in Table V. The specific $D(M^+-CO)$ terms of the tetracarbonyl dimers reveal a trend of alternating low and high energies and this could perhaps be meaningful in suggesting the mechanism of decarbonylation. Assuming that decarbonylation occurs via terminal carbonyls, since the higher energy unbridged isomers of **2** and **3** are likely to be favored under electron-impact conditions, the indicated trend might suggest the complete decarbonylation of each metallic site at a time, rather than the rupture of subsequent carbonyl groups from alternate sites. This proposed decarbonylation scheme is consistent with the general trend of considerably greater energetics required in order to dissociate subsequent carbonyl groups off the same metallic center in various monometallic carbonyl complexes. For instance, such a trend has been observed for complexes of the type $\phi Mn(CO)_n$ [e.g., $\phi Mn(CO)_3$ (ϕ = cyclopentadienyl,[15,16] methylcyclopentadienyl,[16] pyrrolyl,[17] indenyl,[17] fluorenyl[17]), $CpCo(CO)_2$,[15] $CpV(CO)_4$,[15] $R_4C_4Fe(CO)_3$ (R = H,[18] CH_3,[17] Ph[17]), etc.] The mean metal-to-carbonyl bond dissociation energies $[\bar{D}(M^+-CO)]$ in **1**, Q = Cp (0.95 eV), **2** (1.28 eV), and **3** (1.00 eV) are consistently lower than those of the pure monometallic carbonyl complexes of the respective transition elements: $Cr(CO)_6$ (1.4 eV),[19] $Fe(CO)_5$ (1.4 eV),[19] $Ni(CO)_4$ (1.6 eV).[19] In part, this could be due to the high π-acidity character of the cyclopentadienyl ligand. The effect of the cyclopentadienyl ligand on the metal-to-carbonyl bond strength can be demonstrated by comparing the $\bar{D}(Cr^+-CO)$ terms of **1**, Q = Cp, and **1**, Q = C_5Me_5. The π acidity of the permethylated ligand is expected to be considerably lower than that of the parent ligand due to the inductive effect exerted by the methyl substituents. Accordingly, the chromium-to-carbonyl bonds in **1**, Q = C_5Me_5, are expected to be stronger than those in the parent complex **1**; Q = Cp. This conclusion is consistent with $\bar{D}(Cr^+-CO)$ values of 1.61 and 0.95 eV for **1**, Q = C_5Me_5, and **1**, Q = Cp, respectively (Table V). Insofar as the presumed π-acidity order of $C_5H_5 > C_5Me_5$ is concerned, this may also be inferred by comparing the IP of the chromium complexes. The IP of the analogous chromium complexes **1**, Q = Cp, and **1**, Q = C_5Me_5, should depend on the relative σ-basicity:π-acidity ratio of the Q ligand;[20] an increase in the ratio should be concomitant with a decrease in the IP of the complex. The significantly lower IP of **1**, Q = C_5Me_5 (5.89

eV), compared with that of **1**; Q = Cp (6.74 eV), is therefore consistent with the assigned π-acidity order of the ligands ($C_5H_5 > C_5Me_5$). This π-acidity order could perhaps account for the significantly greater abundance of dipositive ions in the mass spectrum of the permethylated analogue.

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Resonance Raman Spectra and Excitation Profiles of Tris(α-diimine) Complexes of Iron(II)

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Measurements of the excitation profiles of six bands of the $[Fe(bmi)_3]^{2+}$ ion, eight bands of the $[Fe(bpy)_3]^{2+}$ ion, and thirteen bands of the $[Fe(phen)_3]^{2+}$ ion in aqueous solution have indicated that the shoulder on the high-frequency side of the main electronic bands of these ions in the visible region is a vibronic side band. For the first ion, the principal fundamental involved is that at 1400 cm⁻¹, for the second ion that at 1607 cm⁻¹, and for the third ion that at 1635 cm⁻¹. The resonance Raman spectra of the ions are dominated by bands arising from totally symmetric fundamentals and this indicates that only one electronic transition (the resonant one) is primarily responsible for the intensity of the Raman emission from these ions with excitation lines in the visible region.

Introduction

All α-diimine ligands can be represented by the general formula
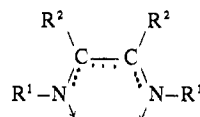
where R^1 and R^2 may be H, alkyl, or phenyl groups. These substituents can also be connected, e.g., in the cases of 2,-2'-bipyridyl and 1,10-phenanthroline. The ligands form tris complexes with iron(II) which are characterized by their high stability and intense absorption in the visible region.[1] The complex ions of iron(II) which are the subject of this investigation are those of the ligands 2,2'-bipyridyl, 1,10-phenanthroline, and biacetyl bis(*N*-methylimine), viz. [Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, and [Fe(bmi)₃]²⁺. The visible absorption spectra of these three ions have been extensively studied and the values of λ_{max} and ϵ_{max} for the main peaks are given in Table I.

While it is generally agreed that the strong visible absorption arises from an electronic dipole allowed metal (3d) to ligand (π) charge-transfer transition,[2] what is not certain is whether the unresolved structure on the high-frequency side of the main absorption band (see Figures 5–9) arises from a vibration in an excited state or from other CT transitions. Under D_3

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Table I. Electronic Absorption Maxima of *a*-Diimineiron(II) Complexes[1]

Complex	λ_{max}/nm	$\tilde{\nu}_{max}$/cm⁻¹	$10^{-3}\epsilon_{max}$/ (dm³ mol⁻¹ cm⁻¹)
[Fe(bpy)₃]²⁺	524	19 100	8.7
[Fe(phen)₃]²⁺	510	19 600	11.5
[Fe(bmi)₃]²⁺	568	17 600	10.7

symmetry the degeneracy of the Fe²⁺ d orbitals and the ligand π orbitals is split[3] and there is thus the possibility of $^1E \leftarrow {}^1A_1$ or $^1A_2 \leftarrow {}^1A_1$ transitions. MO calculations have been performed for all systems[4-7] and in every case but one[7] indicate that only a single transition of the type $^1E \leftarrow {}^1A_1$ should contribute significantly to the absorption spectrum in the visible region. It was therefore proposed that the unresolved structure in the shoulder was mainly due to vibrational progressions[4-8] with only small contributions from other CT transitions. The positions and oscillator strengths of these additional transitions vary widely from paper to paper and due to the uncertainty in the frequency and intensity of the vibrational progression, if any, it is difficult to decide which analysis is most accurate.

Single-crystal polarized absorption studies[9] on the compound [Fe(bpy)₃]SO₄ have also shown that the main absorption band and the shoulder arose almost entirely from $^1E \leftarrow {}^1A_1$ transitions. The results of low-temperature studies on the absorption spectra of compounds containing the [Fe(bpy)₃]²⁺ and [Fe(phen)₃]²⁺ ions suggest that the wavenumbers of the