cyclopentadienyl proton resonance for the complex assigned as $CpFe(CO)(PPh_3)SCN$ but did not influence the chemical shift of this resonance for $CpFe(CO)(PPh_3)NCS$. This behavior is characteristic of thiocyanato organometallic compounds since the N atom of the S-bonded ligand readily coordinates to europium but the S atom of the N-bonded ligand does not.[41]

(41) S. J. Anderson and A. H. Norbury, *J. Chem. Soc., Chem. Commun.*, 48 (1975).

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Mass Spectra of Organometallic Compounds. 7.[1] Electron-Impact Study of Some Cyclopentadienylmetal Thiocarbonyl-Bridged Dimers

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Mass spectra of the thiocarbonyl-bridged dimers $[QMn(CS)(NO)]_2$ ($Q = \eta^5\text{-}C_5H_5$ and $\eta^5\text{-}MeC_5H_4$), $[(\eta^5\text{-}C_5H_5)Fe(CS)(CO)]_2$, and $(\eta^5\text{-}C_5H_5)_2Fe_2(CS)(CO)_3$ have been examined, and appearance potentials of most of the metal-containing fragment ions, especially those with intact ligands, have been determined. The primary fragmentations in the mass spectra of these complexes have been assigned and compared. Fragment ions resulting from the loss of CO or NO are much more abundant than those resulting from the loss of CS. In fact, a large fraction of the total ion current in the mass spectra of those complexes arises from $M_2(CS)_n$-containing ions.

Introduction

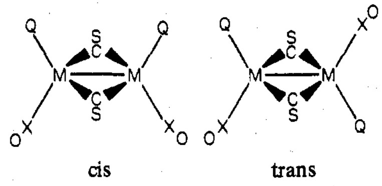
In recent years, a considerable amout of information has become available on the behavior of organometallic compounds under electron-impact conditions.[2] Despite the large volume of mass spectral data on such systems, relatively little effort has been made to examine in detail proposed fragmentation modes. In general, under electron-impact conditions most metal-containing ions exhibit one detectable appearance potential, and this probably suggests the existence of a single primary precursor for each of these ions. An accurate description of a fragmentation pathway should contain viable information concerning predominant processes by which fragment ions are being produced. As a matter of convenience, such processes will henceforth be referred to as primary fragmentations, and this in order to distinguish them from minor processes to be termed secondary. In a primary fragmentation sequence, subsequent ions are expected to exhibit higher appearance potentials due to the endothermicity of the breaking processes involved. Generally, metal-containing ions with all ligands account for most of the ion current in the majority of the mass spectra of organometallic compounds. This feature indicates that under electron-impact conditions the cleavage of metal-to-ligand bonds is greatly favored over processes involving the decay of coordinated ligands. Detailed studies of the energetics of metal-to-ligand bond-breaking fragmentations have so far been reported for relatively few organometallic systems.[1,3]

Recently, we have reported a comprehensive mass spectral study[4] on the well-known cyclopentadienylmetal dimers $[CpCr(CO)_2]_2$, $[Me_5C_5Cr(CO)_2]_2$, $[CpFe(CO)_2]_2$, and $[CpNi(CO)]_2$. A related class of the novel binuclear complexes $[MeC_5H_4Mn(CS)(NO)]_2$,[5] $[CpMn(CS)(NO)]_2$,[5] $[CpFe(CS)(CO)]_2$,[6] and $Cp_2Fe_2(CS)(CO)_3$,[7a] is of considerable interest in view of the remarkably high tendency of the coordinated thiocarbonyl to engage in carbon-bridging geometries.[7b] Incidentally, this tendency is dramatically greater than that of either the carbonyl or the nitrosyl ligands. A detailed analysis of the mass spectra of the carbon-bridged thiocarbonyl derivatives, described in the current paper, was undertaken in order to ascertain their primary fragmentation modes under electron-impact conditions and, more specifically, to examine the influence of this unique bridging ligand on the fragmentation pattern of the complexes. The complexes investigated are known to exist in both cis and trans isomeric forms and have the general structures shown:

Table I. *Intensities* (I) (at 80 eV) and Appearance Potentials (AP) of Metal-Containing Ions in the Mass Spectra of $Q_2Mn_2(CS)_2(NO)_2$ [1: $Q = C_5H_5, CH_3C_5H_4$]

	$Q = C_5H_5$			$Q = CH_3C_5H_4$	
ion	m/z	I,[a] %	AP,[b] eV	m/z	I,[a] %
Metal-Containing Ions with All Ligands					
$Q_2Mn_2(CS)_2(NO)_2^+$	388	40	6.77 ± 0.02	416	61
$Q_2Mn_2(CS)_2(NO)^+$	358	10	7.90 ± 0.02	386	12
$Q_2Mn_2(CS)_2^+$	328	69	8.99 ± 0.02	356	100
$Q_2Mn_2(CS)(NO)^+$	314	2		342	9
$QMn_2(CS)_2(NO)^+$	293	11	11.97 ± 0.02	307	1
$Q_2Mn_2(CS)^+$	284	18	12.64 ± 0.02	312	6
$QMn_2(CS)_2^+$	263	77	12.89 ± 0.02	277	36
$QMn(CS)_2(NO)^+$	238	35	9.03 ± 0.04	252	34
$QMn_2(CS)^+$	219	8	16.18 ± 0.07	233	8
$QMn(CS)_2^+$	208	9	16.02 ± 0.05	222	8
$Mn_2(CS)_2^+$	198	8	20.92 ± 0.04	198	5
$QMn(CS)(NO)^+$	194	8	11.04 ± 0.03	208	6
Q_2Mn^+	185	49	16.16 ± 0.03	213	11
$QMn(CS)^+$	164	27	13.00 ± 0.02	178	12
$(C_5H_5)Mn_2^+$				175	29
QMn^+	120	73	21.33 ± 0.16[c]	134	20
Mn_2^+	110	7	28.38 ± 0.02	110	3
$Mn(CS)^+$	99	5		99	2
Mn^+	55	100	26.71 ± 0.03	55	17
Metal-Containing Ions with Partial Ligands ($I \geqslant 4\%$)					
$(Q - H)Mn_2(CS)_2^+$	262	60	11.87 ± 0.03	276	62
$(Q - H)Mn(CS)_2^+$	207	10	15.61 ± 0.16		
$(C_5H_4)Mn_2^+$	174	23		174	9

[a] Conditions: SHT, 200 ± 2 °C; ICT, 200 ± 2 °C. [b] Conditions: SHT, 165 ± 2 °C; ICT, 200 ± 2 °C. [c] Nitrogen used as calibrant.



cis trans

1, M = Mn; X = N; $Q = C_5H_5, CH_3C_5H_4$
2, M = Fe; X = C; $Q = C_5H_5$

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Table II. Intensities (I) (at 80 eV) and Appearance Potentials (AP) of the Metal-Containing Ions in the Mass Spectra of $Cp_2Fe_2(CS)_2(CO)_2$ (**2**) and $Cp_2Fe_2(CS)(CO)_3$ (**3**)

		$Cp_2Fe_2(CS)_2(CO)_2$		$Cp_2Fe_2(CS)(CO)_3$	
m/z	ion	I,[a] %	AP,[b] eV	I,[c] %	AP,[b] eV
		Metal-Containing Ions with All Ligands			
386	$Cp_2Fe_2(CS)_2(CO)_2^+$	30	6.76 ± 0.04		
370	$Cp_2Fe_2(CS)(CO)_3^+$			14	6.46 ± 0.02
358	$Cp_2Fe_2(CS)_2(CO)^+$	15	7.47 ± 0.02		
342	$Cp_2Fe_2(CS)(CO)_2^+$			30	7.62 ± 0.02
330	$Cp_2Fe_2(CS)_2^+$	100	8.89 ± 0.03		
314	$Cp_2Fe_2(CS)(CO)^+$			36	8.58 ± 0.02
286	$Cp_2Fe_2(CS)^+$	12	12.61 ± 0.04	100	10.44 ± 0.04
265	$CpFe_2(CS)_2^+$	17	13.23 ± 0.02		
242	$Cp_2Fe_2^+$	1		1	
221	$CpFe_2(CS)^+$	20	17.19 ± 0.02	8	16.79 ± 0.02
209	$CpFe(CS)_2^+$	3			
200	$Fe_2(CS)_2^+$	3	22.53 ± 0.03[d]		
193	$CpFe(CS)(CO)^+$	2	13.83 ± 0.11[d]	1	13.13 ± 0.03[d]
186	Cp_2Fe^+	25	8.62 ± 0.03[d]	57	9.03 ± 0.03[d]
177	$CpFe_2^+$	2		1	
165	$CpFe(CS)^+$	9	14.74 ± 0.09[d]	9	14.74 ± 0.04[d]
156	$Fe_2(CS)^+$	3	20.00 ± 0.03[d]	2	26.00 ± 0.03[d]
149	$CpFe(CO)^+$	2		3	
144	$Fe(CS)_2^+$	20			
121	$CpFe^+$	38	15.32 ± 0.03[d]	48	15.82 ± 0.03[d]
112	Fe_2^+	5	20.89 ± 0.03[d]	6	26.71 ± 0.06[d]
100	$Fe(CS)^+$	6	12.02 ± 0.06[d]	5	11.88 ± 0.03[d]
56	Fe^+	17	20.21 ± 0.03[d]	22	20.94 ± 0.03[d]
		Metal-Containing Ions with Partial Ligands ($I \geqslant 4\%$)			
296	$(C_5H_4)_2Fe_2(CS)C^+$	36			
285	$(C_5H_4)CpFe_2(CS)^+$	13			
264	$(C_5H_4)Fe_2(CS)_2^+$	27			
241	$(C_5H_4)CpFe_2^+$	6			
209	$CpFe_2S^+$			6	
208		10	$[(C_5H_4)Fe(CS)_2^+]$	25	$[(C_5H_4)Fe_2S^+]$
176	$(C_5H_4)Fe_2^+$	17			
169		12		9	
152		5			
144	Fe_2S^+			19	
95	$(C_3H_3)Fe^+$	4		6	

[a] Conditions: SHT, 160 ± 2 °C; ICT, 200 ± 2 °C. [b] Conditions: SHT, 145 ± 2 °C; ICT, 200 ± 2 °C. [c] Conditions: SHT, 150 ± 2 °C; ICT, 200 ± 2 °C. [d] Nitrogen used as calibrant.

Experimental Section

The binuclear complexes $[QMn(CS)(NO)]_2$ (**1**: Q = $CH_3C_5H_4$, Cp),[5] $[CpFe(CS)(CO)]_2$ (**2**),[6] and $Cp_2Fe_2(CS)(CO)_3$ (**3**)[7] were prepared according to reported procedures. The studies were performed on the cis–trans isomeric mixture of the complexes. The mass spectra of the complexes under consideration were measured at 80 eV on a Hitachi RMU-7E mass spectrometer which has been modified with a Keithley 427 current amplifier and a ITT Model F 4074, 16-stage electron multiplier. The samples were introduced directly into the ionization chamber of the mass spectrometer under a low pressure of ~10^{-6} Torr. The conditions [sample heater temperature (SHT) and ionization chamber temperature (ICT)] utilized in obtaining the spectra are specified in Tables I and II, as appropriate. Intensities (I) of metal-containing ions (Tables I and II), those containing the most abundant isotopes of the elements involved, are given relative to an arbitrary value 100 chosen for the base peak, that of the most intense peak in each spectrum. Ions having high m/z values were determined with the aid of perfluorokerosene (PFK) standard. Peak patterns due to the characteristic isotopic distribution of elements helped in recognizing many of the fragment ions, especially in the spectra of the iron derivatives. Metastable transitions observed in the spectra of the manganese complexes are listed in Table III.

The ionization and appearance potentials, reported in Tables I and II, were determined by a modified Honig method[8] according to the procedure[9] of Lossing, Tickner, and Bryce, using either benzene (i = 9.44 eV) or nitrogen (i = 15.60 eV) as calibrant.[10] The appearance potential of each ion was measured at least three times independently, and the precision of the mean result is indicated by the quoted standard deviation. The accuracy of the results could not be judged unambiguously; however, it is probably 1 order of magnitude lower than the indicated precision.

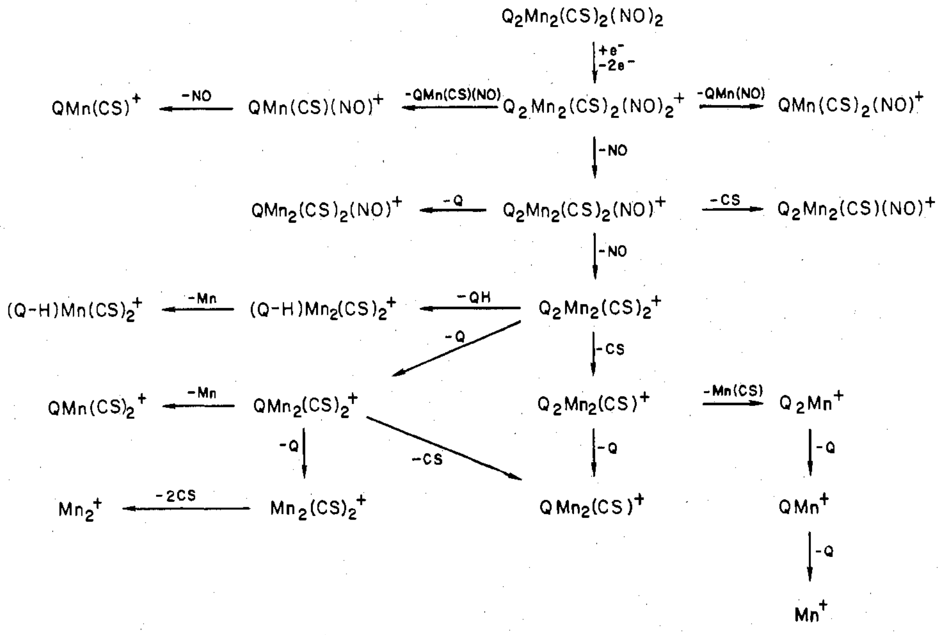
Table III. Metastable Transitions (M*) Found in the Mass Spectra of $Q_2Mn_2(CS)_2(NO)_2$ [**1**: Q = C_5H_5, $CH_3C_5H_4$]

	M* (found)	
process	Q = C_5H_5	Q = $CH_3C_5H_4$
$Q_2Mn_2(CS)_2(NO)_2^+ \rightarrow Q_2Mn_2(CS)_2(NO)^+ + NO$	330.3 m	358.2 s
$Q_2Mn_2(CS)_2(NO)^+ \rightarrow Q_2Mn_2(CS)_2^+ + NO$	300.5 vw	328.3 m
$Q_2Mn_2(CS)_2^+ \rightarrow QMn_2(CS)_2^+ + Q$	210.9 w	215.5 m
$Q_2Mn_2(CS)^+ \rightarrow QMn_2(CS)^+ + Q$	168.9 vw	174.0 w
$(CH_3C_5H_4)Mn_2(CS)_2^+ \rightarrow (CH_3C_5H_4)Mn_2(CS)^+ + CS$		196.0 w

Results and Discussion

$Q_2Mn_2(CS)_2(NO)_2$ Complexes. Intensities and appearance potentials of the metal-containing ions, in particular those with intact ligands, found in the mass spectra of the manganese derivatives $Q_2Mn_2(CS)_2(NO)_2$ [**1**: Q = $CH_3C_5H_4$, Cp] are given in Table I, and metastable transitions are listed in Table III. Primary fragmentations in these spectra, assigned by carefully considering the appearance potential data, are described in Scheme I. First to be considered are those fragmentations which proceed via bimetallic ions. The molecular ion of **1** undergoes a two-step unimolecular nitrosyl dissociation sequence to the nitrosyl-free ion $Q_2Mn_2(CS_2)^+$, which then degrades to $Q_2Mn_2(CS)^+$ by thiocarbonyl dissociation. The rupture of the remaining coordinated thiocarbonyl from the latter ion appears to be greatly unfavored

Scheme I. Primary Fragmentations Proposed in the Mass Spectrum (at 80 eV) of $Q_2Mn_2(CS)_2(NO)_2$ [**1**: Q = Cp, $CH_3C_5H_4$]

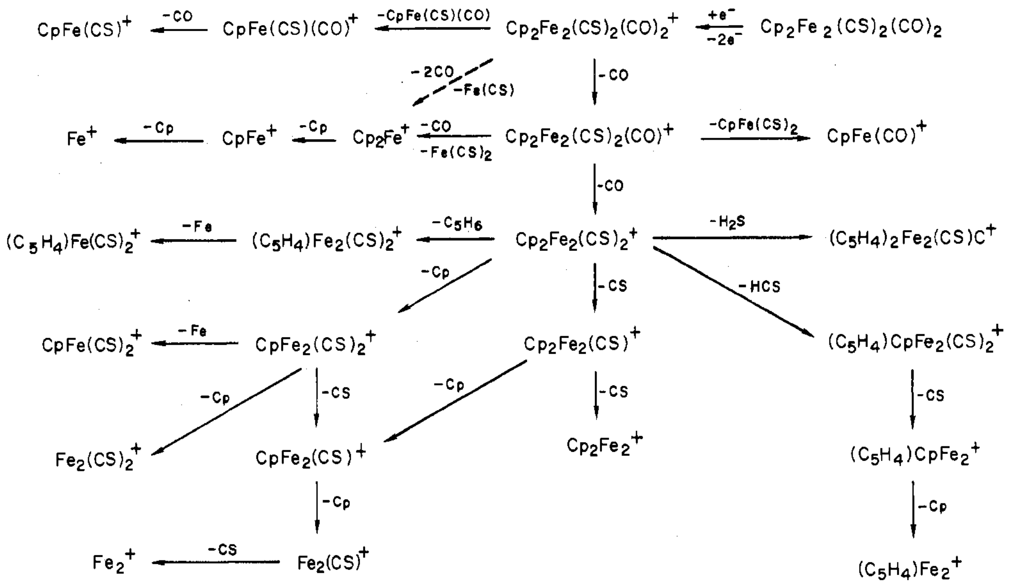


as evident by the absence of $Q_2Mn_2^+$ from the spectra of **1** (Q = $CH_3C_5H_4$, Cp). The low abundance of the bimetallic ions $Q_2Mn_2(CS)(NO)^+$ and $QMn_2(CS)_2(NO)^+$, both presumably originating from $Q_2Mn_2(CS)_2(NO)^+$, suggests that the dissociation of coordinated nitrosyl prior to the rupture of either thiocarbonyl or cyclopentadienyl, though possible, is of relatively low probability. Prominent fragmentations of bimetallic ions are those involving cyclopentadienyl elimination. The formation of $QMn_2(CS)_2^+$ and $QMn_2(CS)^+$ by the rupture of cyclopentadienyl from $Q_2Mn_2(CS)_2^+$ and $Q_2Mn_2(CS)^+$, respectively, is supported in both instances by the appearance potential data as well as the presence of the appropriate metastable transitions. It should, however, be pointed out that the primary route for the production of $QMn_2(CS)^+$ is not entirely certain, since a competitive process to that cited above which involves thiocarbonyl elimination from $QMn_2(CS)_2^+$ is also consistent with the mass spectral data (Tables I and III). The rupture of cyclopentadienyl from $QMn_2(CS)_2^+$ would account for the formation of $Mn_2(CS)_2^+$ [AP, 20.92 eV], and the simultaneous loss of two thiocarbonyl groups from the latter ion is compatible with the production of Mn_2^+ [AP, 28.38 eV] at a rather high potential. Incidentally, the dissociation of Mn_2^+ to Mn^+ by neutral manganese atom elimination could be ruled out in view of the lower appearance potential of the latter ion. In the mass spectra of the manganese derivatives the intense peaks at m/z 262 [**1**, Q = Cp; I = 60%] and 276 [**1**, Q = $CH_3C_5H_4$; I = 62%] have tentatively been assigned to $(Q - H)Mn_2(CS)_2^+$. The formation of these ions by the direct dehydrogenation of $QMn_2(CS)_2^+$ can be ruled out due to the somewhat higher appearance potential of the former ion. A reasonable process to explain the formation of the dehydrogenated ions is envisaged to involve an intramolecular hydrogen transfer followed by cyclopentadiene elimination: $Q_2Mn_2(CS)_2^+ \rightarrow (Q - H)Mn_2(CS)_2^+ + (Q + H)$. The appropriate appearance potential data of **1** (Q = Cp) reveals that the energetics of the presumed cyclopentadiene elimination from $Cp_2Mn_2(CS)_2^+$ [2.88 eV] is smaller, but not greatly different, than those associated with the cyclopentadienyl elimination from either $Cp_2Mn_2(CS)_2^+$ [3.9 eV] or $Cp_2Mn_2(CS)^+$ [3.59 eV].

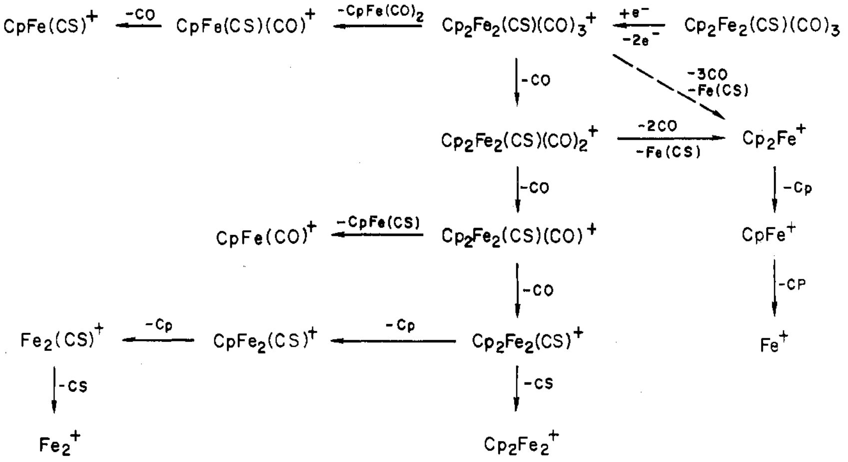
Apart from bimetallic fragmentation sequences, the mass spectra of the manganese derivatives (**1**) show the presence of considerable amounts of various monometallic ions, whose formation and further decay will be considered next. The molecular ion in **1** undergoes symmetric and asymmetric cleavage to afford $QMn(CS)(NO)^+$ and $QMn(CS)_2(NO)^+$, respectively. Although formation of these ions by the cleavage of $Q_2Mn_2(CS)_2(NO)^+$ could not be ruled out, it appears to be of lower probability in view of the significantly higher abundance of the molecular ion. It should also be pointed out that the formation of the half molecular ion by thiocarbonyl dissociation from $QMn(CS)_2(NO)^+$ is totally incompatible with the appearance potentials of the respective ions. Nitrosyl dissociation from $QMn(CS)(NO)^+$ neatly explains the formation of $QMn(CS)^+$; an alternative route to this ion by the dethiocarbonylation of $QMn(CS)_2^+$ can be excluded by considering the appearance potentials of the respective ions. In tracing the origin of $QMn(CS)_2^+$, the denitrosylation of $QMn(CS)_2(NO)^+$ was first to be considered. Evidently, the energetics of ~7 eV suggested for such a process from the appropriate appearance potential data is considerably greater than the more acceptable values in the range of 1–2 eV estimated for nitrosyl dissociation via bimetallic ions. On the basis of energetics of fragmentations, a more viable route to explain the formation of $QMn(CS)_2^+$ is envisaged to involve a neutral manganese atom elimination from $QMn_2(CS)_2^+$. The plausibility of this fragmentation mode is supported by the detection of an analogous process of similar energetics with the bimetallic ions containing the partially dehydrogenated ligand: $(Q - H)Mn_2(CS)_2^+ \rightarrow (Q - H)Mn(CS)_2^+ + Mn$. Manganocenium ($Q_2Mn^+$) and the ions QMn^+ and Mn^+, which are presumed to be derived by its decay, represent the fragmentation sequence of the highest ion current among monometallic ions in the mass spectra of the manganese derivatives (**1**). The formation of the manganocenium will be discussed elsewhere in this paper.

$Cp_2Fe_2(CS)_2(CO)_2$ and $Cp_2Fe(CS)(CO)_3$ Complexes. Intensities and appearance potentials of the metal-containing ions, in particular those with intact ligands, found in the mass spectra of the iron derivatives $Cp_2Fe_2(CS)_2(CO)_2$ (**2**) and $Cp_2Fe_2(CS)(CO)_3$ (**3**) are given in Table II. Primary fragmentations in these spectra are described in Schemes II (**2**) and III (**3**). At the outset, it is noteworthy that many of the fragmentations of bimetallic ions in the mass spectra of the iron derivatives are similar to those described earlier for the manganese system. This may be attributed to the presence of similar structural features in the complexes under consideration, as well as to the comparable energies which are

Scheme II. Primary Fragmentations Proposed in the Mass Spectrum (at 80 eV) of $Cp_2Fe_2(CS)_2(NO)_2$ (**2**)



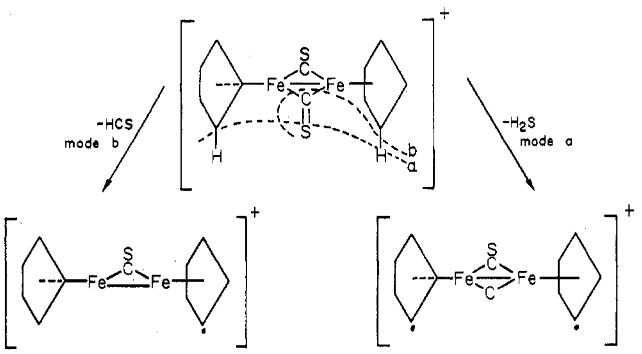
Scheme III. Primary Fragmentations Proposed in the Mass Spectrum (at 80 eV) of $Cp_2Fe_2(CS)(CO)_3$ (**3**)



required to dissociate the coordinated nitrosyl and carbonyl groups. For instance, on the basis of the energetics of the process

$$Cp_2M_2(CS)_2(XO)_2^+ \rightarrow Cp_2M_2(CS)_2^+ + 2XO$$
$$[M = Fe, X = C; M = Mn, X = N]$$

the mean iron-to-carbonyl and manganese-to-nitrosyl ionic bond dissociation energies can be estimated as 1.06 and 1.11 eV, respectively. These values and the mean iron-to-carbonyl ionic bond dissociation energy estimated from the three-step unimolecular carbonyl dissociation sequence of **3** [1.33 eV] appear to differ by relatively little. Several noteworthy differences are found among the fragmentations of bimetallic ions in the spectra of the complexes (**1**, **2**, and **3**). The detection of small amounts of $Cp_2Fe_2^+$ in the spectra of both **2** and **3** contrasts with the failure to observe similar ions in the spectra of the manganese derivatives. Two unique fragmentations involving bimetallic ions have been encountered in the spectrum of **2**. A rather intense peak at *m/z* 296 (I = 37%) in the spectrum of this iron complex has been attributed to the presence of $(C_5H_4)_2Fe_2(CS)C^+$ which is probably formed by H_2S elimination from $Cp_2Fe_2(CS)_2^+$. In a somewhat related process, the carbonyl-free ion $Cp_2Fe_2(CS)_2^+$ appears to undergo a process of HCS elimination to afford $(C_5H_4)CpFe_2(CS)^+$ [*m/z* 285; I = 13%] which then degrades further to $(C_5H_4)Fe_2^+$ [*m/z* 176; I = 17%] via $(C_5H_4)CpFe_2^+$ [*m/z* 241; I = 6%]. It appears almost certain that $(C_5H_4)CpFe_2(CS)^+$ is not produced by the partial dehydrogenation of $Cp_2Fe_2(CS)^+$, since data in support of such a process could not be found in the spectrum of **3** where the latter ion is the base peak. Plausible mechanisms to explain the elimination of H_2S and HCS from $Cp_2Fe_2(CS)_2^+$ are depicted below.



A feature of interest in the bimetallic pathway pertains to the formation of Fe_2^+ in the spectra of **2** [AP, 20.89 eV] and **3** [AP, 26.71 eV]. In both spectra, the appearance potential of $Fe_2(CS)^+$ is somewhat lower than that of Fe_2^+ as would be expected for a genuine precursor. Incidentally, the production of Fe_2^+ by the simultaneous dethiocarbonylation of $Fe_2(CS)_2^+$ in the instance of **2** can be ruled out in view of the significantly higher appearance potential of the latter ion.

The origin of the bimetallic ions $CpFe_2S^+$ [$I = 6\%$] and $(C_5H_4)Fe_2S^+$ [$I = 25\%$] in the mass spectrum of **3** could not be traced with certainty. Evidently, the absence of these ions from the mass spectrum of **2** precludes common bimetallic ions found in both spectra as viable precursors. Carbon atom elimination from coordinated thiocarbonyl can be envisaged to involve cleavage of end-to-end bridging ions according to

$$\text{(ligands)Fe—S{=}C—Fe(ligands)}^+ \rightarrow \text{(ligands)FeS}^+ + \text{(ligands)FeC}$$

Nevertheless, such a process is not valid in the current instance since the integrity of the bimetallic nature of the ions is retained. The presence of Fe_2S^+ [$I = 19\%$] in the spectrum of **3** and its absence from the spectrum of **2** suggests that this ion forms by the decyclopentadienylation of QFe_2S^+ [Q = C_5H_5 or C_5H_4].

Some monometallic ions found in the spectra of **2** and **3** appear to be derived by processes similar to those cited earlier in the instance of **1**. The symmetric cleavage of the molecular ion in **2** and the cleavage of the molecular ion in **3** have been presumed to afford $CpFe(CS)(CO)^+$ which decays by carbonyl dissociation to $CpFe(CS)^+$. A low-intensity peak at m/z 149 in the spectra of **2** [$I = 2\%$] and **3** [$I = 3\%$] has been attributed to the presence of $CpFe(CO)^+$. The precursors of this ion in the spectra of **2** and **3** are suggested to be the bimetallic ions $Cp_2Fe_2(CS)_2(CO)^+$ [$-CpFe(CS)_2$] and $Cp_2Fe_2(CS)(CO)^+$ [$-CpFe(CS)$], respectively, rather than $CpFe(CS)(CO)^+$ [$-CS$] which is also found in both spectra. Circumstantial evidence in support of these assignments comes from the absence of a similar ion $QMn(CO)^+$ in the mass spectra of $QMn(CS)(CO)_2$,[11] where Q = $CH_3C_5H_4$ and Cp.

Formation of Metallocenium Ions. The metalloceniums in the mass spectra of **1**, **2**, and **3** and the ions derived by their decay constitute a major fraction of the ion-current of monometallic ions. The appearance potentials of the overall processes described by eq 1 and 2 can be broken into individual steps whose heat of reaction (ΔH) might be expressed in terms of bond dissociation energies (D). Individual steps are presumed endothermic or exothermic depending on whether bonds are being cleaved or formed, respectively. Ions formed under electron-impact conditions could be considered neither at ground state nor under standard conditions. It should, however, be of interest to make a crude approximation and solve for $\Delta H(1)$ and $\Delta H(2)$ by using estimates of metal-to-ligand bond dissociation energies which were determined from mass spectral data. Estimates of $\Delta H(1a)$ [~ 3.54 eV], $\Delta H(2a)$ [~ 1.42 eV], and $\Delta H(2b)$ [~ 4.34 eV] can be obtained from the appropriate appearance potential data furnished in Tables I and II. Furthermore, estimates of $\Delta H(1c)$ [~ 3.8 eV] and $\Delta H(2d)$ [~ 6.6 eV] are those determined from the mass spectral data of manganocene[3,12] and ferrocene,[3,12] respectively. Direct estimates of the terms $\Delta H(1b)$ and $\Delta H(2c)$ could not be obtained from the appearance potential data of **1** and **2**. In a formal sense, processes 1b and 2c only involve cleavage of a metal–metal bond. Accordingly, the decay of $CpM_2(CS)_2^+$ to either $CpM^+ + M(CS)_2$ or $CpM(CS)_2^+ + M$ should proceed via similar energetics; similar considerations should also apply to the decay of $CpM_2(CS)^+$ to either $CpM^+ + M(CS)$ or $CpM(CS)^+ + M$. The only fragmentations which permit the evaluation of the energetics of such processes can be found in the instance of the manganese complex **1**: $CpMn_2(CS)_2^+ \rightarrow CpMn(CS)_2^+ + Mn$ [3.13 eV] and $(C_5H_4)Mn_2(CS)_2^+ \rightarrow (C_5H_4)Mn(CS)_2^+ + Mn$ [3.74 eV]. In the absence of better estimates, the average value of 3.4 eV will be considered representative for the terms $D(Mn^+ - Mn)$ and $D(Fe^+ - Fe)$. On the basis of estimates of $\Delta H(1a)$, $\Delta H(1b)$, and $\Delta H(1c)$ and $\Delta H(2a)$, $\Delta H(2b)$, $\Delta H(2c)$, and $\Delta H(2d)$, and the overall terms $\Delta H(1)$ [~ 3.14 eV] and $\Delta H(2)$ [~ 1.85 eV] yield the appearance potentials 15.78 eV for Cp_2Mn^+ (found, 16.10 eV) and 10.03 eV for Cp_2Fe^+ (found, 8.62 eV). These considerations appear to support the formation of the metalloceniums in **1** and **2** by processes involving the simultaneous cyclopentadienyl transfer and $M(CS)_n$ elimination.

$$Cp_2Mn_2(CS)^+ \rightarrow CpMn_2(CS)^+ + Cp \tag{1a}$$

$$\Delta H(1a) = D(Mn^+ - Cp)$$

$$CpMn_2(CS) \rightarrow CpMn^+ + Mn(CS) \tag{1b}$$

$$\Delta H(1b) = D(Mn^+ - Mn)$$

$$CpMn^+ + Cp \rightarrow Cp_2Mn^+ \tag{1c}$$

$$\Delta H(1c) = -D(CpMn^+ - Cp)$$

$$Cp_2Mn_2(CS)^+ \rightarrow Cp_2Mn^+ + Mn(CS) \tag{1}$$

$$\Delta H(1) = D(Mn^+ - Cp) + D(Mn^+ - Mn) - D(CpMn^+ - Cp)$$

$$Cp_2Fe_2(CS)_2(CO)^+ \rightarrow Cp_2Fe_2(CS)_2^+ + CO \tag{2a}$$

$$\Delta H(2a) = D(Fe^+ - CO)$$

$$Cp_2Fe_2(CS)_2^+ \rightarrow CpFe_2(CS)_2^+ + Cp \tag{2b}$$

$$\Delta H(2b) = D(Fe^+ - Cp)$$

$$CpFe_2(CS)_2^+ \rightarrow CpFe^+ + Fe(CS)_2 \tag{2c}$$

$$\Delta H(2c) = D(Fe^+ - Fe)$$

$$CpFe^+ + Cp \rightarrow Cp_2Fe^+ \tag{2d}$$

$$\Delta H(2d) = -D(CpFe^+ - Cp)$$

$$Cp_2Fe_2(CS)_2(CO) \rightarrow Cp_2Fe^+ + Fe(CS)_2 + CO \tag{2}$$

$$\Delta H(2) = D(Fe^+ - CO) + D(Fe^+ - Cp) + D(Fe^+ - Fe) - D(CpFe^+ - Cp)$$

Conclusion

Some brief comments should be made concerning the effects of bridging thiocarbonyl ligands on the modes of binuclear complex fragmentation. A large fraction of the total ion-current in the mass spectra of these complexes consists of $M_2(CS)_n$-containing ions. Except for the production of metalloceniums by the simultaneous cyclopentadienyl transfer and $M(CS)_n$ elimination processes, the cleavage of the $M_2(CS)_n$-containing ions is not a particularly favored process as evidenced by the relatively low ion-current of the monometallic ions. By contrast with the facile carbonyl and nitrosyl dissociation processes, fragmentations involving the rupture of a coordinated thiocarbonyl are not common. In fact, fragmentations such as those involving metal–metal bond cleavage proceed via the elimination of either a neutral metal atom or a neutral $M(CS)_n$-containing fragment, and these would suggest the high tendency exhibited by the thiocarbonyl group to remain in a coordinated state. The presence of $QMn(CS)_2(NO)^+$ ions in mass spectra of **1** (Q = Cp and $CH_3C_5H_4$) and the persistence of the $M_2(CS)_n$ ions in the spectra of all three complexes suggest the possibility that at least some of the bimetallic ions might contain a thiocarbonyl-bridged geometry.

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Registry No. **1** (Q = $CH_3C_5H_4$), 64090-74-0; **1** (Q = Cp), 64090-73-9; **2**, 67225-86-9; **3**, 67113-80-8.

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Nickel Atom–Olefin Chemistry. Investigation of the Optical Spectra of Binary Nickel–Olefin Complexes

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Cocondensation of nickel atoms with simple alkyl, fluoro, or chloro olefins, in the temperature range 10–77 K, has resulted in a large series of binary π complexes of the type $Ni(ol)_n$ (where $n = 1$–3). A characteristic feature of these complexes is an intense absorption in the ultraviolet. This transition is only slightly sensitive to the substituent(s) on the coordinated olefin but highly sensitive to the number of coordinated olefins. Observed trends in the optical spectra are interpreted in terms of electronic transitions mainly localized on the nickel atom, and a correlation is observed between the transition energies of the mono(olefin)nickel complexes and the π^* orbital energy of the free olefin. Similar results have been obtained with a variety of palladium–olefin cocondensations. The complexes show a fair degree of thermal stability in the matrices studied. This, coupled with the absence of any evidence of oxidative addition, implies the metal-atom technique may be a general tool for the synthesis of such transition-metal π complexes.

Introduction

The study of transition-metal olefin complexes, with an eye toward understanding the effect on the metal–olefin bond of substituents on the olefin, has utilized a wide variety of techniques. These include measuring IR frequencies (and force constants),[1,2] NMR chemical shifts and coupling constants,[3] thermodynamic stability constants from olefin-displacement/competition reactions,[4-6] and crystallographic bond lengths and angle data for coordinated olefins,[7] among others.

Ittel[2] recently examined the effect of olefin substituents by measuring the changes in $\nu(C{\equiv}N)$ stretching frequencies in compounds of the type $Ni(t\text{-}BuNC)_2(ol)$. He determined that substituent effects were cumulative and that the electron-withdrawal properties of the olefins were relatively inductive in nature, while the overall bond strengths were more closely related to resonance effects. Tolman[3] showed that the upfield chemical shifts of ^{13}C NMR resonances of coordinated olefins were an indication of the degree of π-electron density back-bonded from the metal to the olefin, with more highly activated olefins or electron-rich metals causing greater upfield shifts. Tolman[4] has also investigated the reactions of olefins with $Ni[P(O\text{-}o\text{-}tol)_3]_3$ to form $Ni[P(O\text{-}o\text{-}tol)_3]_2(ol)$ complexes, determining the equilibrium constants spectrophotometrically. It was found that electron-withdrawing substituents on acyclic olefins gave more stable olefin complexes, with resonance effects more important than inductive effects. In a similar study,[5,6] nickel–olefin complexes of the types $Ni(bpy)(ol)$ and $R_2Ni(bpy)(ol)$ were investigated and from their stability constants, it was determined that the π-acceptor capacity rather than σ-donor ability of the olefin was the more important factor in the formation of stable nickel–olefin bonds.

While all of these studies have provided interesting insights into the metal–olefin bond, it must be recognized that in all cases discussed to date, other ligands besides the olefin under consideration were by necessity bonded to the central metal atom. Hence extraneous ligand electronic and geometric effects on the metal–olefin bond under study were sometimes difficult to evaluate. Up until now, there has been a distinct absence of data[8] of a systematic nature concerning simple binary metal–olefin complexes, consideration of which would obviate concern about these effects. In fact, in the case of nickel there is still a great deal of work to be done with binary mono(olefin) complexes, as very few have actually been synthesized.[9] For this reason and in view of our previous success with the cryochemical synthesis of such complexes as $Ni(ol)_{1,2,3}$ where ol is C_2H_4[10] and C_2F_4,[11] we have set out to synthesize a wide variety of new nickel–olefin complexes.

A characteristic spectral feature of the binary nickel–olefin complexes turned out to be an intense absorption in the ultraviolet, one band being associated with each compound. This transition, particularly in the case of the mono(olefin) complexes, shows a *small but distinct sensitivity* to the substituents on the coordinated olefin. By reference to molecular orbital calculations of the extended-Hückel[12] and SCF-Xα-SW[13] types, as well as to optical data for discrete metal–olefin complexes,[8] these intense UV absorptions have been previously assigned as metal-to-ligand charge-transfer (MLCT) transitions between closely spaced levels of the nickel(0) d-orbital manifold and empty orbitals centered mainly on the olefins involving contributions from the olefin π^* antibonding and symmetry-related $Ni(d_\pi)$ levels. The current study suggests that this is not an exact description.

Thus, by concentrating on a wide variety of binary nickel–olefin complexes, albeit on a matrix scale, we are able to overcome the difficulties associated with unwanted ligand effects, either electronic or steric, on the properties under study, and by concentrating on their UV spectra we can in principle gain a unique insight into the electronic and bonding properties of the metal–olefin bond.

Experimental Section

Monoatomic Ni and Pd vapors were generated by directly heating a 0.015-in. ribbon filament of the metal with ac in a furnace similar to that described previously.[14] The nickel (99.99%) and palladium (99.99%) were supplied by McKay, N.Y., Gaseous olefins were

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