$Mo^{VI}O_2^{2+}$ group is nearly as effective as a proton at electron withdrawing. Hence, the molybdenum–ligand oxygen interaction has significant covalent character, which is in accord with the interpretations of the proton NMR data for this complex.[5]

Reference to Table II indicates that the chemical shift differences between $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ for C4, C5, and C8 (12.0, 8.8, and −11.8 ppm, respectively) provide a sensitive measure of the nature of the metal–ligand bonding relative to that for the zinc 4-methyl-8-quinolinate complex. These three resonances should be useful diagnostic probes for the bonding of other metal–4MQ complexes, especially with respect to the degree of covalent character of the metal–ligand oxygen bond.

Because only a single set of ligand resonances is observed for each of the $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ complexes, the two ligands of each complex must be equivalent. Although this is in accord with the proton NMR results,[5,8] the much greater sensitivity of ^{13}C NMR to shielding effects adds convincing support for the conclusion that the ligands are symmetrical to each other in the $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ complexes.

Acknowledgment. This project was initiated several years ago through the use of a locally fabricated ^{13}C NMR spectrometer. Although the instrument's sensitivity proved inadequate, the efforts and contributions of J. L. Sudmeier, L. J. DeHayes, and P. C. Curb are gratefully acknowledged. The work was supported by the National Science Foundation under Grants CHE 76-24555 and CHE 79-22040.

Registry No. HQ, 148-24-3; 2MQH, 826-81-3; H1N, 90-15-3; $4MQH_2^+$, 73940-74-6; 4MQH, 3846-73-9; $4MQ^-$, 35489-22-6; $Zn(4MQ)_2$, 14406-95-2; $MoO_2(4MQ)_2$, 73953-19-2.

Contribution from the Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel, and the School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903

Mass Spectra of Organometallic Compounds. 8.[1] Electron-Impact Study of the Cyclopentadienylmanganese Derivatives $RC_5H_4Mn(CS)(NO)I$ ($R = H, CH_3$)

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The mass spectra of the related cyclopentadienylmanganese complexes $RC_5H_4Mn(CS)(NO)I$ ($R = H, CH_3$) have been examined, and the appearance potentials of manganese-containing ions with intact ligands determined. Primary fragmentations in the mass spectra of these complexes have been assigned and compared. The strength of the manganese-to-ligand bonds in the fragment ions was shown to follow the order $I > RC_5H_4 > CS \gg NO$.

Introduction

Appearance potentials of ions produced under electron-impact conditions provide valuable information concerning fragmentation processes. In general, metal-containing ions with all ligands account for most of the ion current in the majority of the spectra of organometallic compounds. This feature indicates that under electron-impact conditions the cleavage of metal-to-ligand bonds is greatly favored over fragmentations involving the decay of coordinated ligands. Most metal-containing ions in the mass spectra of organometallic compounds exhibit one detectable appearance potential, and this probably suggests the existence of a single primary precursor for each of the ions. In a fragmentation sequence proceeding via primary precursors, subsequent ions are expected to exhibit higher appearance potentials due to the endothermicity of the bond-breaking processes involved. Except for the detailed study of fragmentation sequences, appearance potentials also furnish valuable information concerning the energetics of such processes.

The behavior of coordinated ligands under electron-impact conditions is of considerable importance in the understanding of the mass spectra of organometallic compounds. A detailed comparison between the behavior of several ligands has been investigated in the mass spectral study of $RC_5H_4Mn(CO)(CS)L$ [$L = CO, Ph_3P, Ph_3As, Ph_3Sb$; $R = H, CH_3$].[2,3] A recently reported mass spectral study of the novel binuclear complexes $[RC_5H_4Mn(CS)(NO)]_2$ ($R = H, CH_3$) and $[C_5H_5Fe(CS)(CO)]_2$ brought into focus the behavior of carbon-bridging thiocarbonyl as compared with those of the terminal nitrosyl and carbonyl ligands, respectively. A detailed analysis of the mass spectra of $RC_5H_4Mn(CS)(NO)I$ ($R = H, CH_3$), described in the current paper, was undertaken in order to obtain a meaningful comparison between the behavior of the terminal thiocarbonyl and nitrosyl ligands under electron-impact conditions.

Experimental Section

The complexes $RC_5H_4Mn(CS)(NO)I$ ($R = H, CH_3$) were prepared according to a reported procedure.[4] 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 $\sim 10^{-6}$ torr. The conditions [sample heater temperature (SHT) and ionization chamber temperature (ICT)] utilized in obtaining the spectra are specified in Table I. Intensities (I) of the ions (Table I), those containing the most abundant isotopes of the elements involved, are given relative to an arbitrary value of 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. Metastable transitions observed in the spectra of the manganese complexes are listed in Table I.

The ionization and appearance potentials, reported in Table I, were determined by a modified Honig method[5] according to the procedure[6]

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Table I. Intensities (I) (at 80 eV) and Appearance Potentials (AP) of the Metal-Containing Ions, Organic Ions, and Metastable Transitions (M*) in the Mass Spectra of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3)

	R = H			R = CH_3		
ion	m/z	I,[a] %	AP,[b] eV	m/z	I,[a] %	AP,[c] eV
Metal-Containing Ions with All Ligands						
$RC_5H_4Mn(CS)(NO)I^+$	321	65	7.45 ± 0.02	335	89	7.35 ± 0.02
$RC_5H_4Mn(CS)I^+$	291	89	8.81 ± 0.02	305	94	8.90 ± 0.02
$RC_5H_4MnI^+$	247	55	10.92 ± 0.03	261	100.0	10.93 ± 0.02
$Mn(CS)I^+$	226	34	13.97 ± 0.03	226	20	14.91 ± 0.04
$RC_5H_4Mn(CS)(NO)^+$	194	7	8.77 ± 0.04	208	3	8.68 ± 0.02
MnI^+	182	79	16.15 ± 0.04	182	52	17.11 ± 0.03
$RC_5H_4Mn(CS)^+$	164	18	10.17 ± 0.03	178	5	10.21 ± 0.03
$RC_5H_4Mn^+$	120	100	12.84 ± 0.03	134	26	13.19 ± 0.04
$Mn(CS)^+$	99	6	17.74 ± 0.03[d]	99	2	18.00 ± 0.05[d]
Mn^+	55	78	16.57 ± 0.03[d]	55	22	15.57 ± 0.07[d]

Organic and Metal-Containing Ions with Partial Ligands ($I \geqslant 2\%$)

m/z (I,[a] %, ion) R = H: 127 (3, I^+), 109 (9, $C_6H_5S^+$), 93 (4, $C_3H_2Mn^+$), 80 (7, C_2HMn^+), 66 (4, $C_5H_6^+$), 65 (5, $C_5H_5^+$), 39 (13, $C_3H_3^+$)

m/z (I,[a] %, ion) R = CH_3: 321 (2, $C_5H_5Mn(CS)(NO)I^+$), 319 (2, $C_5H_3Mn(CS)(NO)I^+$), 291 (2, $C_5H_5Mn(CS)I^+$), 289 (4, $C_5H_3Mn(CS)I^+$), 247 (2, $C_5H_5MnI^+$), 123 (5, $C_7H_7S^+$), 93 (3, $C_3H_2Mn^+$), 84 (4, $C_2H_5Mn^+$), 80 (6, C_2HMn^+), 79 (35, $C_6H_7^+$), 78 (5, $C_6H_6^+$), 77 (10, $C_6H_5^+$), 76 (7, $C_6H_4^+$), 39 (2, $C_3H_3^+$)

Metastable Transitions (M^*)

$RC_5H_4Mn(CS)(NO)I^+ \rightarrow RC_5H_4Mn(CS)I^+ + NO$	R = H; M^* = 263.80 (s) R = CH_3; M^* = 278.28 (m)
$C_5H_5Mn(CS)I^+ \rightarrow C_5H_5MnI^+ + CS$	M^* = 208.65 (w)

[a] SHT, 110 ± 2 °C; ICT, 200 ± 2 °C. [b] SHT, 70 ± 2 °C; ICT, 100 ± 2 °C. [c] SHT, 68 ± 2 °C; ICT, 100 ± 2 °C. [d] Nitrogen used as calibrant.

Table II. Relative Currents (RC) (at 80 eV) of Group Ions in the Mass Spectra of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3)

	RC,[a] %	
type of group ions	R = H	R = CH_3
Mn containing (total)	95	87
Mn(I) containing with all ligands	56	62
Mn(CS) containing with all ligands	38	42
Mn(NO) containing with all ligands	13	18
$Mn(RC_5H_4)$ containing with all ligands	58	63
Mn containing with partial ligands	2	5
organic	5	13

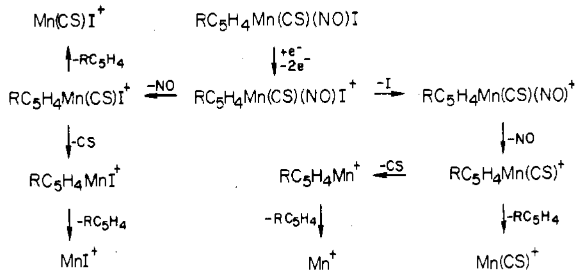
[a] Computed from $[\Sigma I_i/I_t] \times 100$, where ΣI_i is the sum of intensities of the group ions type i and I_t is the sum of intensities of all of the ions in the spectrum.

of Lossing, Tickner, andd Bryce, using either benzene (i = 9.44 eV) or nitrogen (i = 15.60 eV) as calibrant.[7] 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 an order of magnitude lower than the indicated precision.

Results and Discussion

Intensities, appearance potentials, and metastable transitions of manganese-containing ions, in particular those with intact ligands, found in the mass spectra of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3) are given in Table I. Relative currents of group ions in the mass spectra of these complexes are listed in Table II. Several noteworthy conclusions can be reached on the basis of the information furnished in Table II. Most of the ion currents in these spectra originate from manganese-containing ions with all ligands. Currents due organic ions [RC: 5% (R = H); 13% (R = CH_3)] and manganese-containing ions with partial ligands [RC: 2% (R = H); 5% (R = CH_3)] are quite low. Currents of group ions with intact ligands decrease in the order Mn(I) > $Mn(RC_5H_4)$ > Mn(CS) > Mn(NO). Most probably, this order reflects the tendency of the ligands to survive fragmentation off the manganese atom under electron-impact conditions. It should, however, be pointed out that deiodination processes appear to become greatly unfavored only beyond the first step by which $RC_5H_4Mn(CS)(NO)^+$ is formed. The facile deiodination of the molecular ion might in part be due to release of steric strain which arises from nonbonding repulsive interactions of the ligands around the manganese atom.

Scheme I. Primary Fragmentations Proposed in the Mass Spectra (at 80 eV) of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3)



The primary fragmentations of manganese-containing ions with intact ligands in the mass spectra of $RC_5H_4Mn(CS)(NO)I$ ($R = H_3CH_3$) are proposed in Scheme I. The molecular ion undergoes either nitrosyl or iodine elimination to afford $RC_5H_4Mn(CS)I^+$ and $RC_5H_4Mn(CS)(NO)^+$, respectively. On the basis of the appearance potentials of the parent and daughter ions, both of these processes proceed via similar energetics (range, 1.32–1.55 eV). The denitrosylation of the molecular ion is supported in both mass spectra by the presence of the appropriate metastable transitions (Table I). In light of the high current of Mn(I)-containing ions, it has been assumed that deiodination processes do not play a major role in the decay of $RC_5H_4Mn(CS)I^+$. Therefore, it is proposed that this ion degrades by two main pathways: (a) a two-step sequence involving the elimination of thiocarbonyl and cyclopentadienyl to give $RC_5H_4MnI^+$ and MnI^+, respectively, and (b) the elimination of cyclopentadienyl to afford $Mn(CS)I^+$. Since the probability of formation of $RC_5H_4MnI^+$ by a low-energy pathway (2.03–2.11 eV) is considerably greater than that of Mn(CS)I (5.16–6.01 eV), the subsequent decay of the former ion represents a more viable route in the formation of MnI^+.

Fragmentation of the iodine-free ions is initiated by the denitrosylation of $RC_5H_4Mn(CS)(NO)^+$ a process by which $RC_5H_4Mn(CS)^+$ is formed. The resulting ion fragments further by losing either thiocarbonyl or cyclopentadienyl to give $RC_5H_4Mn^+$ and $Mn(CS)^+$, respectively. The production of the former ion is of considerably higher probability since its formation involves a significantly lower energy pathway. Bare manganese ions in the mass spectra under consideration arise by the decyclopentadienylation of $RC_5H_4Mn^+$ rather than by the alternative process of thiocarbonyl elimination from $Mn(CS)^+$. This assignment is supported by the significantly higher appearance potential of the latter ion [17.74 eV (R = H), 18.00 eV (R = CH_3)] as compared with that of Mn^+ [16.37 eV (R = H), 15.57 eV (R = CH_3)]. It should also be pointed out that the appearance potential of MnI^+ [16.15 eV (R = H), 17.11 eV (R = CH_3)] is either about the same or somewhat higher than that of Mn^+, and this would exclude

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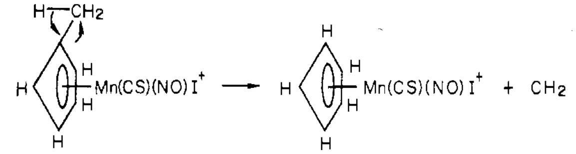
(7) J. Roboz "Introduction to Mass Spectrometry, Instrumentation and Techniques", Interscience, New York, 1968, Appendix II, p 515.

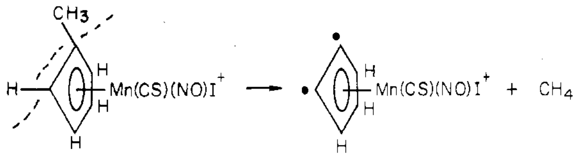
the former ion from being a genuine precursor of the formation of the latter.

Apart from fragmentation involving all ligands, some noteworthy fragmentations via metal-containing ions with partial ligands have also been observed in the mass spectrum of $CH_3C_5H_4Mn(CS)(NO)I$. The ion having $m/z = 329$ ($I = 2\%$) in this spectrum, assigned structure $C_5H_5Mn(CS)(NO)I^+$, is presumed to be formed by an intramolecular process involving hydrogen transfer and methylene elimination (eq I). Degradation of this ion according to the sequence



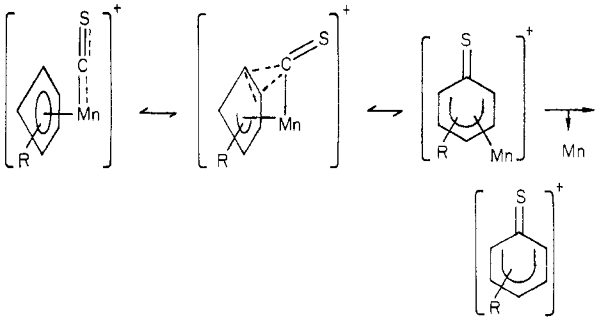
(I)

proposed for the Mn(I)-containing ions in Scheme I is indicated by the low abundance (I ~2%) of $C_5H_5Mn(CS)I$ ($m/z = 291$) and $C_5H_5MnI^+$ ($m/z = 247$). Another fragmentation initiated with the molecular ion is that involving the formation of $C_5H_3Mn(CS)(NO)I^+$, probably by a process involving methane elimination (eq II). In this instance, the nearest subsequent ion that of $C_5H_3Mn(CS)I^+$ ($m/z = 289$) could also be detected.



(II)

Certain of the organic ions in the mass spectra under consideration also deserve some attention. Both spectra exhibit the appropriate peaks for $RC_5H_4^+$ and $RC_5H_5^+$ as might be expected. Of particular interest are the peaks at $m/z = 109$ ($I = 7\%$) and 123 ($I = 5\%$) which correspond to $RC_5H_4(CS)^+$, where R = H and CH_3, respectively. Although the origin of this ion could not be traced with certainty, it appears as if these ions arise from an intramolecular insertion of a coordinated thiocarbonyl into the cyclopentadienyl ligand. A speculative mechanism which might explain the formation of this ion, starting with $RC_5H_4Mn(CS)^+$, is shown in eq III.



(III)

Conclusion

The primary fragmentations in the mass spectra of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3), investigated in this work, bring into light the relative behavior of certain coordinated ligands under electron-impact conditions. Except in the instance of the molecular ion, the rupture of Mn–I bonds appears to be the least favored process in the system under investigation. Dissociation of coordinated thiocarbonyl is energetically greatly favored over the elimination of the cyclopentadienyl ligand. Dissociation of cyclopentadienyl prior to thiocarbonyl, although possible, involves processes of a rather low probability. Cleavage of the nitrosyl ligand appears to be the most facile fragmentation in the system under consideration. The foregoing suggests that Mn^+–L bond strength in fragment ions follows the order $L = I > RC_5H_4 > CS \gg NO$. This order is consistent with the decrease in the relative currents of group ions; $Mn(I) \sim Mn(RC_5H_4) > Mn(CS) > Mn(NO)$.

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Registry No. $C_5H_5Mn(CS)(NO)I$, 58450-74-1; $CH_3C_5H_4Mn(CS)(NO)I$, 64057-05-2.