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## MASS SPECTROMETRY OF TRANSITION-METAL $\pi$ -COMPLEXES

### IV \*. A STUDY OF SOME DERIVATIVES OF CYCLOHEPTADIENYLTRICARBONYLMANGANESE

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#### Summary

The mass spectral fragmentation of (cyclo-6-*exo*-C<sub>7</sub>H<sub>5</sub>R)Mn(CO)<sub>3</sub>, (R = H, CN; OMe, OEt, O-*t*-Bu, NHMe, NPh) has been examined. When R = H or CN, complete decarbonylation precedes any fragmentation of the organic ligand. For the other complexes, the only process able to compete with decarbonylation of the molecular ion is loss of R<sup>•</sup>. Such behaviour is discussed in terms of charge localisation effects.

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#### Introduction

In an earlier publication [2], one of us discussed the mass spectral fragmentation of transition metal  $\pi$ -complexes in terms of charge localisation and its consequences. In that paper, it was suggested that fragmentation of organometallic molecular ions by loss of small neutral molecules such as H<sub>2</sub>, rather than by the loss of radicals such as H<sup>•</sup>, reflects not only the relative activation energies of the processes in question but also the fact that the metal atom may act as the site of charge localisation. Thus in molecular ions of complexes of the type LM(CO)<sub>3</sub> (L = a  $\pi$ -bonded organic ligand), charge localisation at the metal atom means that the electronic configuration of the ligand L may well be different to that of the free-ligand molecular ion, L<sup>+</sup>. For example, if L is an even-electron ligand, perhaps a diene, then it can maintain its even-electron nature in LM(CO)<sub>3</sub><sup>+</sup>, whereas L<sup>+</sup> will, of necessity, be odd-electron. If the approach suggested by McLafferty [3] is then applied to these ions, the molecular ion of the free ligand may be expected to undergo preferential radical loss producing

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an even-electron daughter ion, while the complexed ligand in decomposing from an even-electron situation (with respect to the organic moiety) may yield an even-electron neutral and retain the even-electron character of the organic moiety in the metal-bonded daughter ion. However, this approach is purely a rationale of the results quoted in ref. 2 and on that basis there is no means of assessing the relative importance of activation energies and charge localisation. Here we present a study of cycloheptadienyltricarbonylmanganese and some of its derivatives which yields a better insight into these two effects.

## Results and discussion

In seeking to test the importance of relative activation energies versus charge localisation effects on the fragmentation of the molecular ions of metal-bonded organic ligands we have examined the mass spectra of (cyclo-6-*exo*-C<sub>7</sub>H<sub>8</sub>R)Mn(CO)<sub>3</sub> (I, R = H; II, R = OCH<sub>3</sub>; III, R = OC<sub>2</sub>H<sub>5</sub>; IV, R = OC(CH<sub>3</sub>)<sub>3</sub>; V, R = NHCH<sub>3</sub>; VI, R = NHC<sub>6</sub>H<sub>5</sub>; VII, R = CN). As the organic ligand is a five- $\pi$  system, ionisation involving an electron of predominantly metal character will maintain the odd-electron configuration of the organic ligand. If fragmentation of the organic ligand is solely governed by activation energy considerations, then the only processes able to compete with decarbonylation of the molecular ion will be loss of H<sub>2</sub> or RH from C(6) and C(7). That is, the fragmentation will be exactly analogous to that of derivatives of cyclohexadienetricarbonyliron [2,4]. If, however, electronic configuration is of some importance, then the organic moiety might expel a radical, R $\cdot$  or H $\cdot$ , thereby achieving an even-electron configuration.

The molecular ions of all complexes show decarbonylation as their principal route of decomposition. In the case of I, no fragmentation of the organic ligand is observed until all carbonyl groups have been lost. A similar situation was observed for (cyclo-C<sub>6</sub>H<sub>8</sub>)Fe(CO)<sub>3</sub> [6] in which formation of [C<sub>6</sub>H<sub>6</sub>Fe(CO)<sub>n</sub>]<sup>+</sup> was only observed for n = 1 and 0, and for (cyclo-C<sub>7</sub>H<sub>7</sub>X)V(CO)<sub>3</sub> (X = H, Me,

TABLE 1  
MASS SPECTRUM OF I

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
232	23.1	232 → 204
204	14.6	204 → 176
176	12.3	176 → 148
148	100.0	148 → 146
146	31.5	148 → 92
93	11.5	148 → 56
92	10.0	146 → 91
91	87.7	93 → 91
80	10.8	91 → 65
77	18.5	
65	15.4	
57	11.5	
56	42.3	
55	96.2	
43	13.1	
41	16.2	
39	17.7	

TABLE 2  
MASS SPECTRUM OF II

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
262	3.8	262 → 234
234	4.6	234 → 206
231	2.0	206 → 178
206	6.2	178 → 148
203	2.4	178 → 123
178	18.4	148 → 147
175	10.3	148 → 146
148	10.3	148 → 92
147	4.9	148 → 56
146	19.5	146 → 91
123	15.4	123 → 91
121	4.6	91 → 65
120	5.1	
119	5.1	
106	18.4	
105	20.0	
92	32.4	
91	100.0	
85	9.2	
77	11.6	
65	29.5	
57	43.2	
55	55.4	
43	54.1	
39	29.2	

TABLE 3  
MASS SPECTRUM OF III

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
276	10.9	276 → 248
248	4.7	248 → 220
231	2.5	231 → 203
220	8.8	220 → 192
203	2.0	203 → 175
192	37.5	192 → 148
175	4.5	192 → 137
148	34.4	148 → 146
147	10.0	148 → 92
146	18.1	148 → 56
137	33.4	146 → 120
120	5.3	146 → 91
109	6.3	137 → 109
107	9.8	137 → 91
100	22.8	91 → 65
92	18.5	
91	93.8	
80	13.6	
79	11.3	
77	10.9	
69	20.8	
65	25.3	
56	50.0	
55	100.0	
41	10.0	
39	24.7	

TABLE 4  
MASS SPECTRUM OF IV

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
304	10.3	304 → 276
276	3.2	276 → 248
248	10.0	248 → 220
231	4.2	231 → 203
220	16.1	220 → 164
203	1.2	203 → 175
175	3.2	175 → 147
164	35.5	164 → 163
163	7.1	164 → 162
162	35.5	164 → 147
147	11.0	146 → 91
146	12.5	91 → 65
128	67.7	
121	8.7	
110	11.0	
108	8.4	
92	25.5	
91	93.6	
80	12.4	
79	10.7	
77	11.2	
65	26.1	
63	9.4	
59	22.1	
57	45.2	
56	38.7	
55	100.0	
43	26.5	
41	64.5	
39	45.2	

Ph) which showed loss of H<sub>2</sub> from [(C<sub>7</sub>H<sub>6</sub>X)V]<sup>+</sup> [7] [(C<sub>7</sub>H<sub>9</sub>)Mn]<sup>+</sup> (*m/e* 148) shows three routes of decomposition which are supported by metastable ions. These are: (a) loss of H<sub>2</sub>, (b) formation of MnH<sup>+</sup> and (c) formation of C<sub>7</sub>H<sub>8</sub><sup>+</sup>, of which (a) is the most important. This might be expected for an ion which has undergone three successive decarbonylation reactions each of which will reduce the internal energy of the daughter ion such that only fragmentations of low activation energy are observed [5].

The three alkoxy derivatives (II, III and IV) all show a second route for decomposition of the molecular ion accompanying decarbonylation. In each case this involves loss of OR<sup>•</sup> (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>9</sub>). The resulting ion, [C<sub>7</sub>H<sub>8</sub>Mn(CO)<sub>3</sub>]<sup>+</sup> undergoes subsequent stepwise elimination of carbon monoxide molecules. None of the three molecular ions shows any loss of H<sub>2</sub>, RH or H<sup>•</sup>. The decarbonylated ions, [(C<sub>7</sub>H<sub>8</sub>OR)Mn]<sup>+</sup> all give rise to the elimination of even-electron neutrals. Thus, for II and III loss of RCHO (R = H, CH<sub>3</sub>) is observed yielding [(C<sub>7</sub>H<sub>9</sub>)Mn]<sup>+</sup> (*m/e* 148) which does not fragment in a manner strictly comparable with that discussed above for I. In addition to the routes outlined for I, H<sup>•</sup> is also lost (metastable observed). The ion [(C<sub>7</sub>H<sub>8</sub>O<sub>*t*</sub>Bu)Mn]<sup>+</sup>, produced

TABLE 5  
MASS SPECTRUM OF V

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
261	2.7	261 → 233
233	5.3	233 → 205
231	1.7	205 → 177
205	5.9	203 → 175
203	1.0	177 → 147
177	11.8	177 → 122
175	2.3	175 → 120
148	3.5	148 → 146
147	3.3	147 → 146
146	3.3	146 → 91
122	100.0	122 → 91
120	27.7	91 → 65
91	43.5	
80	8.2	
77	10.0	
65	14.1	
56	15.3	
55	82.4	
43	9.4	
42	24.7	
41	15.9	
39	19.4	

from IV, being unable to transfer from the  $\alpha$ -carbon atom of the side chain does not show loss of  $C_3H_5O$ , but does eliminate  $C_3H_8$ . A range of structures can be written for the daughter ion of this fragmentation ( $m/e$  164). However, as one route for its decomposition that can be confirmed by the presence of

TABLE 6  
MASS SPECTRUM OF VI

<i>m/e</i>	Relative intensity	Metastable supported fragmentations
323	9.3	323 → 295
295	1.0	295 → 267
267	5.3	267 → 239
239	36.7	231 → 203
237	17.0	239 → 237
231	3.0	239 → 184
211	6.7	239 → 147
203	1.2	237 → 182
184	27.0	
182	26.0	
147	21.3	
106	43.3	
93	21.7	
91	33.4	
77	18.3	
65	7.3	
64	15.3	
63	24.3	
56	22.0	
55	100.0	
41	18.5	
39	32.3	

metastable ions is loss of  $\text{OH}^\cdot$ , it probably has the structure  $[(\text{C}_7\text{H}_8\text{OH})\text{Mn}]^\ddagger$ . If this is the case then the formation of  $m/e$  164 must involve a four-membered transition state. Elimination of  $\text{C}_2\text{H}_4$  from phenetole has also been shown to involve a four-membered transition state [8]. The ion at  $m/e$  164 also shows elimination of  $\text{H}_2$  and loss of  $\text{H}^\cdot$ , both of which are metastable supported.

Both V and VI show loss of  $\text{NHR}^\cdot$  ( $\text{R} = \text{Me}, \text{Ph}$ ) as the only fragmentation able to compete with decarbonylation of the molecular ion. Fragmentation of the decarbonylated ions,  $[(\text{C}_7\text{H}_8\text{NHR})\text{Mn}]^\ddagger$  differs from that of the related alkoxy ions in that both show loss of  $\text{RNH}^\cdot$  as the only metastable supported decomposition other than metal-ligand bond cleavage. The spectrum of V does show an ion at  $m/e$  148 which could arise via  $\text{CH}_2=\text{NH}$  elimination, analogous to that of II, however, there are no metastable ions to support this fragmentation.

The spectrum of VII is extremely simple. The molecular ion fragments only by decarbonylation and the ion  $[(\text{C}_7\text{H}_8\text{CN})\text{Mn}]^\ddagger$  ( $m/e$  173) shows loss of  $\text{HCN}$  as its only route of decomposition (metastable ion observed). The reason for this atypical behaviour is not clear, however, it is interesting to note that 5-*exo*-cyanocyclohexadienetricarbonyliron fragments in a different manner to other compounds of this type [9].

Thus, in summary, molecular ions of the complexes (*cyclo-6-*exo*-C<sub>7</sub>H<sub>8</sub>R*)Mn(CO)<sub>3</sub> ( $\text{R} = \text{MeO}, \text{EtO}, \text{t-BuO}, \text{MeNH}, \text{PhNH}$ ) all show radical loss as the only process able to compete with decarbonylation. The other two complexes studied ( $\text{R} = \text{H}, \text{CN}$ ) show only decarbonylation of the molecular ion. We believe this supports our earlier contention [2], that charge localisation is an important factor in the fragmentation of such ions. Nevertheless, it must be emphasised that there are exceptions to this generalisation, the most notable of which is probably the loss of  $\text{R}^\cdot$  radicals by the molecular ions of some substituted cycloheptatriene complexes, (*7-*exo*-C<sub>7</sub>H<sub>7</sub>R*)Cr(CO)<sub>3</sub> [10]. In these cases, charge transfer from the metal to the fragmenting organic ligand probably occurs in the transition state thereby yielding the  $6\pi$ -tropylium ion coordinated to chromium(0).

TABLE 7  
MASS SPECTRUM OF VII

$m/e$	Relative intensity	Metastable supported fragmentations
257	4.2	257 → 229
229	3.4	229 → 201
201	3.5	201 → 173
173	9.2	173 → 146
146	31.5	146 → 91
118	2.4	146 → 55
116	3.5	
91	88.5	
89	5.0	
81	12.3	
65	18.1	
63	6.9	
56	19.8	
55	100.0	
41	6.1	
39	21.2	

## Experimental

All complexes were prepared by published procedures [11] and gave satisfactory analyses, IR and NMR spectra. Mass spectra were recorded on an AEI MS 9 operating at 70 eV and 100  $\mu$ A trap current. Fragmentation patterns were recorded at 1000 resolution and any ion assignments in question confirmed by mass measurement at 10 000 resolution performed by the peak matching technique.

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