Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

REARRANGEMENT IONS IN THE MASS SPECTRA OF ORGANOMETALLIC COMPOUNDS
THE FORMATION OF INTERMEDIATE π-COMPLEXES

J. D. HAWTHORNE, M. J. MAYS AND R. N. F. SIMPSON
University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)

(Received December 21st, 1967)

A feature of the mass spectra of organometallic compounds is the prominence of ions formed by rearrangement whereby ligand fragments are transferred to the metal atom. Such ions have been reported, for example, in the fragmentation of ferrocene type complexes[1,2] (transfer of ring substituents to the metal atom), in some sulphur-bridged carbonyl complexes[3], and in a series of substituted manganese carbonyls[4]. We report here examples of the formation of these rearrangement ions during the fragmentation of organometallic compounds containing σ-bonded organic ligands, and suggest processes by which the transfer of ligand fragments to the metal atom may occur.

TABLE 1

MASS SPECTRUM OF π-$C_5H_5Mo(CO)_3(CH_2)_3I$

m/e[a]	Ion	A
416	$C_5H_5Mo(CO)_3(CH_2)_3I^+$	3
388	$C_5H_5Mo(CO)_2(CH_2)_3I^+$	27
360	$C_5H_5Mo(CO)(CH_2)_3I^+$	18
332	$C_5H_5Mo(CH_2)_3I^+$	1
318	$C_5H_5Mo(CH_2)_2I^+$	2
304	$C_5H_5Mo(CH_2)I^+$	9
290	$C_5H_5MoI^+$	100
164	$C_5H_5MoH^+$	2
163	$C_5H_5Mo^+$	16
98	Mo^+	4
66	$C_5H_6^+$	2
65	$C_5H_5^+$	3

[a] For ^{98}Mo.

In general, transfer of atoms or groups to a metal atom is favoured both by the formation of new strong bonds to the metal and by the elimination of comparatively stable neutral molecules. Both these criteria are satisfied, for example, in the case of $CF_3Mn(CO)_5$, where ions of the type $FM(CO)_n^+$ ($n = 5 \rightarrow 0$) are major features of the spectrum[4]. The spectrum of π-$C_5H_5Mo(CO)_3(CH_2)_3I$ (Table 1) demonstrates the influence of a sterically favoured transition state. The base peak is π-$C_5H_5MoI^+$, which must have been generated via a five-membered cyclic transition state; a weaker peak at *m/e* 304 (π-$C_5H_5MoCH_2I^+$) presumably arises from an alternative pathway involving elimination of ethylene from π-$C_5H_5Mo(CH_2)_3I^+$. Unfortunately there are no visible metastables to confirm these processes, but no π-$C_5H_5Mo(CO)_3I$ impurity could be detected in the mass spectrum. The formation of the above-mentioned rearrangement ions might have been predicted by analogy with related organic species. Thus the spectrum of trifluoromethylbenzene contains an intense peak at *m/e* 96 due to the ejection of difluoromethylene from the molecular ion[5], and the ion $C_4H_8X^+$, postulated as a five-membered cyclic ion, is a major or base peak in the spectrum of n-alkyl chlorides and bromides[6]. The function of the metal atom in these instances may be little different from that of an adjacent carbon atom. In the case of unsaturated σ-bonded organic ligands, however, rearrangement ions are produced, the formation of which can best be rationalised by assuming that the ligand becomes π-bonded to the metal during fragmentation of the molecular ion. For example our previous studies of fluorine transfer in *ortho*-, *meta*-, and *para*-substituted fluorophenyl manganese pentacarbonyls[4] showed that migration to the metal could occur from all ring positions although it was most favoured from the *ortho*-position.

The above conclusions are reinforced by examination of the fragmentation patterns of several fluorophosphines (Tables 2 and 3). Fluorine transfer to phosphorus from an α- or β-carbon atom occurs readily in $P(C_6F_5)_3$[7] and $P(CF_3)_3$; in

TABLE 2

MASS SPECTRUM OF $P(CF_3)_3$

m/e	Ion	*A*
238	$P(CF_3)_3^{+\cdot}$	50
219	$P(CF_3)_2(CF_2)^+$	73
188	$P(CF_3)_2F^{+\cdot}$	3
169	$P(CF_3)_2^{+\cdot}$	3
150	$P(CF_3)(CF_2)^+$	33
133	—	48
131	$P(CF_2)_2^{+\cdot}$	95
119	$P(CF_3)F^+$	9
114	—	42
100	$P(CF_3)^+$	52
81	$P(CF_2)^+$	26
69	$PF_2^{+\cdot}$	100
	$CF_3^{+\cdot}$	700
62	$PCF^{+\cdot}$	17
50	PF^+, $CF_2^{+\cdot}$	45
31	P^+, CF^+	57

Metastable peaks

94.5 238 → 150+CF_4
78.4 192 → 131+CF_4
41.7 238 → 100+C_2F_6
36.3 69 → 50+F
25.6 150 → 62+CF_4

TABLE 3

MASS SPECTRUM OF $P(C_6H_4$-*p*-$F)_3$

m/e	Ion	*A*
316	$P(C_6H_4F)_3^{+\cdot}$	46
221	$P(C_6H_4F)_2^{+\cdot}$	6
219	$P(C_6H_3F)_2^{+\cdot}$	10
201	$P(C_6H_5F)(C_6H_4)^{+\cdot}$	2
158	—	8
126	$P(C_6H_4F)^+$	100
125	$P(C_6H_3F)^+$	24
75	—	14

Mestastable peaks

150.5 316 → 221+C_6H_4F

the latter case, an analysis of the metastable peaks observed indicates that the occurrence of high abundance ions is governed by an unusual fragmentation process involving the elimination of CF_4 or C_2F_6 as stable neutral species from the molecular ion and its fragments. A similar effect is observed with $As(CF_3)_3$[8]. No ions with fluorine bonded to phosphorus are found, however, in the spectrum of $P(C_6H_4\text{-}p\text{-}F)_3$ (Table 3) where the formation of a suitable π-bonded intermediate is most unlikely.

TABLE 4

MASS SPECTRUM OF $\pi\text{-}C_5H_5Fe(CO)_2CH_2C_6H_4CH_3$

m/e	Ion	*A*
282	$C_5H_5FeC_8H_9(CO)_2^+$	4
254	$C_5H_5FeC_8H_9(CO)^+$	23
226	$C_5H_5FeC_8H_9^+$	100
178	$C_5H_5Fe(CO)_2H^+$	2
177	$C_5H_5Fe(CO)_2^+$	3
150	$C_5H_5Fe(CO)H^+$	4
149	$C_5H_5Fe(CO)^+$	5
122	C_5H_5FeH	5
121	$C_5H_5Fe^+$	27
106	$C_8H_{10}^+$	18
105	$C_8H_9^+$	21
92	$C_7H_8^+$	2
91	$C_7H_7^+$	15
66	$C_5H_6^+$	13
65	$C_5H_5^+$	5
56	Fe^+	4

TABLE 5

MASS SPECTRUM OF $C_6F_5CH_2Mn(CO)_5$

m/e	Ion	*A*
376	$C_6F_5CH_2Mn(CO)_5^+$	35
348	$C_6F_5CH_2Mn(CO)_4^+$	7
329	$C_6F_4CH_2Mn(CO)_4^+$	2
320	$C_6F_5CH_2Mn(CO)_3^+$	1
292	$C_6F_5CH_2Mn(CO)_2^+$	3
273	$C_6F_4CH_2Mn(CO)_2^+$	1
264	$C_6F_5CH_2Mn(CO)^+$	7
245	$C_6F_4CH_2Mn(CO)^+$	2
236	$C_6F_5CH_2Mn^+$	100
215	$C_6F_4CH_2Mn^+$	3
195	$Mn(CO)_5^+$	97
181	$C_6F_5CH_2^+$	240
167	$Mn(CO)_4^+$	41
139	$Mn(CO)_3^+$	34
111	$Mn(CO)_2^+$	22
83	$Mn(CO)^+$	23
74	MnF^+	20
55	Mn^+	91

TABLE 6

MASS SPECTRUM OF $p\text{-}FC_6H_4CH_2Mn(CO)_5$

m/e	Ion	*A*
304	$FC_6H_4CH_2Mn(CO)_5^+$	10
276	$FC_6H_4CH_2Mn(CO)_4^+$	21
248	$FC_6H_4CH_2Mn(CO)_3^+$	7
220	$FC_6H_4CH_2Mn(CO)_2^+$	10
195	$Mn(CO)_5^+$	3
192	$FC_6H_4CH_2Mn(CO)^+$	14
167	$Mn(CO)_4^+$	1
164	$FC_6H_4CH_2Mn^+$	100
139	$Mn(CO)_3^+$	3
111	$Mn(CO)_2^+$	21
110	$FC_6H_4CH_3^+$	186
109	$FC_6H_4CH_2^+$	345
92	$C_7H_8^+$	21
91	$C_7H_7^+$	38
84	$Mn(CO)H^+$	10
83	$Mn(CO)^+$	45
74	MnF^+	17
56	MnH^+	24
55	Mn^+	72

Bruce[9] has recently suggested a similar σ–π rearrangement to explain features of the mass spectrum of an benzyliron compound. We have independently examined the mass spectrum of a number of benzyl complexes and while our results (Tables 4–6) confirm the importance of σ–π rearrangements in some at least of these complexes, we disagree with Bruce's detailed conclusions. The most striking evidence in favour of the σ–π hypothesis is the presence of a prominent peak at *m/e* 74 (MnF^+) in the mass spectrum of p-$FC_6H_4CH_2Mn(CO)_5$. There is also a similar peak in the spectrum of $C_6F_5CH_2Mn(CO)_5$, but since transfer of fluorine from the γ-carbon atom of the σ-bonded ligand is not inconceivable this result does not necessarily imply the formation of a π-bonded intermediate. The exact nature of the π-bonded intermediates in these benzyl compounds is difficult to determine. It has been suggested[9] by analogy with organic systems and on the basis of the intensity of the molecular ion compared to $(M-CO)^+$ and $(M-2\ CO)^+$ that a π-bonded tropylium ion is formed. While this possibility cannot be eliminated the evidence in its favour is not conclusive. Even with organic species this particular rearrangement does not always take place and, for example, the presence of a p-methoxy group in the ring stabilises the benzyl structure[10]. We suggest that similar stabilisation may be achieved in benzylmetal complexes through the formation of a π-allyl intermediate. The formation of such an intermediate has been postulated to explain the high intensity of the $(M-CO)^+$ ion in $(CH_2CN)Mn(CO)_5$[4] and it can equally well be invoked here for $C_5H_5Fe(CO)_2CH_2C_6H_4CH_3$ in which the molecular ion is almost absent. Indeed in the case of π-$C_5H_5Mo(CO)_3CH_2C_6H_5$ the complex π-$C_5H_5Mo(CO)_2(\pi$-$CH_2C_6H_5)$ can actually be isolated upon UV irradiation[11]. The association of high stability with abundance of particular ions is not in general justified, however, because of the numerous competing equilibria involved in fragmentation.

ACKNOWLEDGEMENTS

Research grants from the S.R.C. to J.D.H. and R.N.F.S. are gratefully acknowledged.

REFERENCES

1 A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, (1964) 3847.
2 H. Egger, *Monatsh. Chem.*, 97 (1966) 602.
3 B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc., A*, (1967) 338.
4 M. J. Mays and R. N. F. Simpson, *J. Chem. Soc., A*, (1967) 1936.
5 J. R. Majer, *J. Appl. Chem. (London)*, 11 (1961) 141.
6 F. W. McLafferty, *Anal. Chem.*, 34 (1962) 2.
7 J. M. Miller, *J. Chem. Soc., A*, (1967) 828.
8 R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, 6 (1967) 1450.
9 M. I. Bruce, *J. Organometal. Chem.*, 10 (1967) 495.
10 J. M. S. Tait, T. W. Shannon and A. G. Harrison, *J. Amer. Chem. Soc.*, 84 (1962) 4.
11 R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 88 (1966) 709.