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Electron impact (EI) and fast-atom bombardment (FAB) mass spectra of coordination complexes: aggregation processes in the mass spectra of metal derivatives of 1,2,3,4,5-pentakis-(methoxycarbonyl)cyclopentadiene

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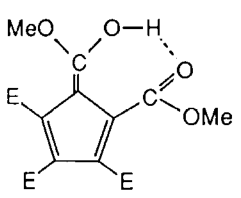
Abstract

The mass spectra of $HC_5(CO_2Me)_5$ [H(cpp)] and several of its metal derivatives have been studied. In the EI mass spectra of alkali metal salts, aggregate ions $[m_2(cpp)]^+$ were observed. The abundance of these and higher oligomers is increased in FAB mass spectra, ions containing up to seven (negative ion) or eight (positive ion) metal atoms being found. Fragmentation patterns were established for the diene and $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}$ by high resolution EI measurements. Unusual replacement of CO_2Me by H (by loss of $CO+CH_2O$) occurred in the latter, eventually to give $[Ru(C_5H_3)(C_5H_5)]^+$.

Introduction

In a recent review describing the utility of fast-atom bombardment (FAB) mass spectrometry to the analysis and characterisation of coordination and organometallic compounds [1], we drew attention to the ion–ion and ion–molecule association reactions that are evidenced by the appearance of ions at higher mass numbers than that of the formal parent (or molecular) ion. These were exemplified by our own experiences with the spectra of metal compounds derived from 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene ($HC_5(CO_2Me)_5$, H(cpp); **1**) on the one hand and of tertiary phosphine derivatives of alkynyl complexes of the Group 11 metals on the other [2]. Others have reported similar features, for example, in the FAB mass spectra of mixed ligand derivatives of magnesium [3], or uranyl acetate and nitrate [4], of acetates of Mg, Hg and Pb [5], of transition metal acetylacetonate complexes [6], of allylpalladium complexes [7] and of $Pt(PPh_3)_4$ [8]. This paper details our findings in studies of the electron impact (EI) and FAB mass spectra of complexes containing the $C_5(CO_2Me)_5$ ligand.



$E = Co_2Me$

Results and discussion

Electron impact (EI) mass spectra

The suggested fragmentation pattern derived from the positive ion EI mass spectrum of $HC_5(CO_2Me)_5$ is shown in Scheme 1. The major fragmentation processes observed include the expected loss of H or CO_2 from the parent ion and of H_2O, CO, CH_2O, OMe and CO_2 from other ions; the proximity of the CO_2Me substituents also results in cyclic elimination processes leading to transfer of H to the ring carbons, i.e. net replacement of CO_2Me by H. However, loss of HCO is also a predominant process, probably resulting from opening of the ring and subsequent fragmentations.

The major ions present in spectra obtained from m(cpp) (m = Li, K, Tl)** and from a mixture of Li(cpp) with Rb(cpp) are listed in Table 1. Ions above the parent ion, although of weak intensity, were readily assigned to aggregates of type $[m_2(cpp)]^+$ and gave the first indication of ion–molecule association processes in these compounds. For example, in the cases of the lithium and potassium salts, where they were found at *m/z* 368/369 (for the $^6Li^7Li/^7Li_2$ ions) and 433/435/437

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**In this paper, the symbol m is used to denote a metal atom, *M* for the molecular ion.

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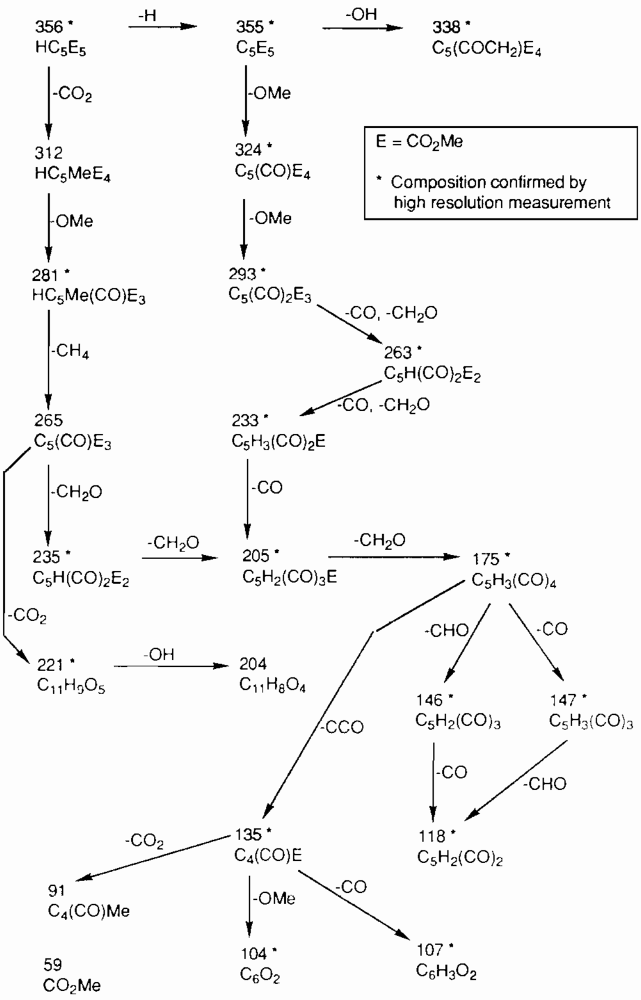


Scheme 1.

TABLE 1. EI mass spectra of m(cpp) (m = Li, K, Tl) and of a 1/1 mixture of Li(cpp) and Rb(cpp)

Ion	^{7}Li^{a}	^{39}K	^{205}Tl^{b}	^{7}Li + ^{85}Rb
Metal containing				
m$_2$(cpp)	369 13.6	433 1.3	763 0.9	Rb$_2$ 0.7 LiRb 3.5 Li$_2$ 7.3
M − OMe	331 2.0	363 2.6	529 25.8	Rb 0.3 Li 8.9
m(cpp)	362	394	560 56.7	Rb 1.6 Li 8.9
Organic	m/z			
$C_{15}H_{14}O_9$	338 2.6	14.3		
$C_{14}H_{12}O_9$	324 2.6	8.6	30.9	30.0
$C_{14}H_{16}O_8$	312 2.7	20.0	2.8	9.1
$C_{13}H_9O_8$	293 8.4	32.9	82.5	100
$C_{13}H_{13}O_7$	281 6.9	100	3.4	20.9
$C_{13}H_{11}O_6$	263 2.6	7.4	11.6	12.3
	249	25.7		12.3
	248	20.0	1.8	13.1
$C_{12}H_{11}O_5$	235 5.8	13.4	7.5	26.8
$C_{11}H_9O_5$	221	14.3		8.6
$C_{10}H_5O_5$	205	20.0		8.6
	182 6.2	20.0		
$C_9H_3O_4$	175 5.1		3.1	7.4
	154 18.2	9.4		
$C_8H_3O_3$	147 27.3	9.1		9.6
$C_7H_3O_3$	135	8.1		
$C_7H_2O_2$	118	4.9	7.7	15.5
	59 81.8	9.1	10.8	20.3

[a] m/z 78 = 100. [b] ^{205}Tl^{+} = 100.

(for the $^{39}K_2$/$^{39}K^{41}K$/$^{41}K_2$ ions), respectively. Interestingly, as Table 1 shows, the mass spectrum of a mixture of salts, e.g. Li(cpp) + Rb(cpp), shows all possible combinations of [mm′(cpp)]$^+$, the ions [$^7Li_2$(cpp)]$^+$, [$^7Li^{85}Rb$(cpp)]$^+$ and [$^{85}Rb_2$(cpp)]$^+$ being found at m/z 369, 447 and 525, respectively (the other isotopic combinations were also observed), together with the corresponding daughter ions formed by loss of CH_2O or OMe. Relatively little fragmentation was found with these compounds, many of the ions being the same as those found in the spectrum of H(cpp). A similar pattern was seen for the thallium(I) derivative.

Fast-atom bombardment (FAB) mass spectra

Table 2 summarises the positive ion FAB mass spectra of the compounds m(cpp) (m = Li, Na, K, Rb, Tl) and Ag(cpp)(PPh_3). The positive ion spectrum of K(cpp) is shown in Fig. 1.

For the alkali metal compounds, it is immediately evident that most spectra contain weak high mass ions which can be formulated as the mono-cations $[M_n(\mathrm{cpp})_{n-1} - \mathrm{OMe}]^+$. Some further fragmentation by loss of Me, OMe or CO_2Me groups is also found. For all the alkali metal salts, $[M_2(\mathrm{cpp})]^+$ is the base peak. The value of n depends upon the alkali metal: for m = Li, aggregates containing up to eight Li atoms are found. As the size of the alkali metal increases, n becomes smaller, although with m = Li and Cs, the ions with $n = 5$ are equally intense. In the negative ion spectrum of K(cpp), ions of the general formula $[K_n(\mathrm{cpp})_{n+1}]^-$ ($n = 1$–8) are present, with relative intensities between 0.05 ($n = 8$) and 100 ($n = 1$); no fragmentation was found. For Li(cpp), only the very intense ions [cpp]$^-$ and $[\mathrm{Li(cpp)_2}]^-$ were recorded.

Similar aggregate ions have been studied extensively in the spectra of alkali metal halides; in which case (CsI) aggregates with up to 100 (positive ion) or 87 Cs atoms (negative ion) have been identified [9]. It is supposed that these compositions reflect the stability of the gas-phase clusters that are formed upon volatilisation of the solid substrate. In the present case, there is an additional driving force which leads to aggregation, namely that resulting from coordination of the ester oxygen atoms to the metal. This is analogous to the extensive interactions found in the solid state

TABLE 2. Positive ion FAB mass spectra of m(cpp) (m = Li, Na, K, Rb, Cs; cpp = C$_5$(CO$_2$Me)$_5$)[a]

Ion	Li		Na		K		Rb		Cs	
m$_8$(cpp)$_4$ − OMe	1445	0.1								
m$_8$(cpp)$_3$ − OMe	1090	0.3								
m$_7$(cpp)$_4$ − OMe	1438	0.1								
m$_7$(cpp)$_3$ − OMe	1083	0.6								
m$_6$(cpp)$_3$ − OMe			1172	0.3	1268	0.04				
m$_5$(cpp)$_3$			1180	0.2						
m$_5$(cpp)$_3$ − Me			1165	0.5	1245	0.15				
m$_5$(cpp)$_2$	745	3							1375	3
m$_5$(cpp)$_2$ − OMe			794	1	874	0.7	1106	0.5		
m$_4$(cpp)$_3$			1157	0.2	1221	0.11				
m$_4$(cpp)$_2$ − Me	723	6	787	4	851	2	1037	1		
m$_4$(cpp)$_2$ − OMe − Me	692	2								
m$_4$(cpp)	383	7								
m$_4$(cpp) − OMe			416	6	480	3	666	2		
m$_3$(cpp)$_2$	731	32	779	13	827	4	967	3	1109	3
m$_3$(cpp)$_2$ − OMe	700	2	748	0.8						
m$_3$(cpp)$_2$ − OMe − Me	685	3	733	2						
m$_3$(cpp)$_2$ − CO$_2$Me	672	2	720	1			908	1		
m$_3$(cpp)$_2$ − CO$_2$Me − OMe − Me	626	0.5							1004	4
m$_3$(cpp) − Me	361	8	409	9	457	21	597	24	739	10
m$_3$(cpp) − CO$_2$Me − Me					398	7	538	7	680	5
m$_2$(cpp)	369	100	401	100	433	100	525	100	621	100
m$_2$(cpp) − Me	354	5					510	6	606	10
m$_2$(cpp) − OMe	338	6	370	5	402	6	494	7	590	6
m$_2$(cpp) − OMe − Me	323	13	355	14	387	19	479	29	575	10
m$_2$(cpp) − CO$_2$Me	310	12	342	10	374	10	466	9	562	8
m$_2$(cpp) − CO$_2$Me − OMe	279	9	311	6						
m$_2$(cpp) − CO$_2$Me − OMe − Me			296	7	328	11	420	8		
m$_2$(cpp) − 2CO$_2$Me	251	2			315	4	407[b]	7		
m$_2$(cpp) − 2CO$_2$Me − OMe	220	2								
m$_2$(cpp) − 2CO$_2$Me − OMe − Me					269	5				
m(cpp)									488	14
m(cpp) − OMe	331	47	347	11	363	7	409[b]	7	457	22
m(cpp) − CO$_2$Me − Me							366	4		
m(cpp) − 2CO$_2$Me − Me					261	7				

[a] *m*/*z* values reported for most abundant metal isotopic combination. [b] Unresolved.

studies: Fig. 2 illustrates the coordination of the K atom in solid K(cpp) [10]. As can be seen, each metal atom interacts with ester O atoms from five CO$_2$Me groups supplied by three cpp anions, as well as with a solvent MeOH molecule. In this way, a complex three-dimensional network is formed. The polynuclear ions seen in the FAB mass spectra may have related structures.

In the spectra of Tl(cpp), the only ions observed were Tl$^+$ (positive ion) and [cpp]$^-$ (negative ion).

The FAB mass spectrum of Ag(cpp)(PPh$_3$) contains an aggregate ion [{Ag(PPh$_3$)}$_2$(cpp)]$^+$ (*m*/*z* 1093) which loses PPh$_3$ to give [Ag$_2$(PPh$_3$)(cpp)]$^+$ as the base peak. These argentated molecular ions are isolobally related to the more common protonated molecular ions. We have discussed their occurrence and formation elsewhere [2]. The remainder of the spectrum is simple, containing M^+, $[M-n\mathrm{OMe}]^+$ ($n = 1$, 3) and [Ag(PPh$_3$)]$^+$.

There has been only limited discussion about the mechanism of formation of aggregate ions similar to those observed in the present study [11]. In general terms, aggregation has been considered to occur in the matrix [12] or within a matrix plasma in the gas phase [13]. Our results here do not serve to clarify further the possible mechanisms which are involved, but the electrostatic cation/anion interaction and coordination opportunities offered suggest that these ions have extended oligomeric structures related to those found in the solid state. It is of interest that the multiple oxygen functionalities present in polysaccharides lead to the formation of particularly stable cluster ions [14].

Mass spectra of Fe(cpp)$_2$ and Ru(cpp)(η-C$_5$H$_5$)

No aggregate ions were found in the FAB mass spectrum of Fe(cpp)$_2$ (Table 2). The positive ion contains ions derived by loss of OMe, Me or CO$_2$Me groups from the molecular ion, at *m*/*z* 766, which lead to

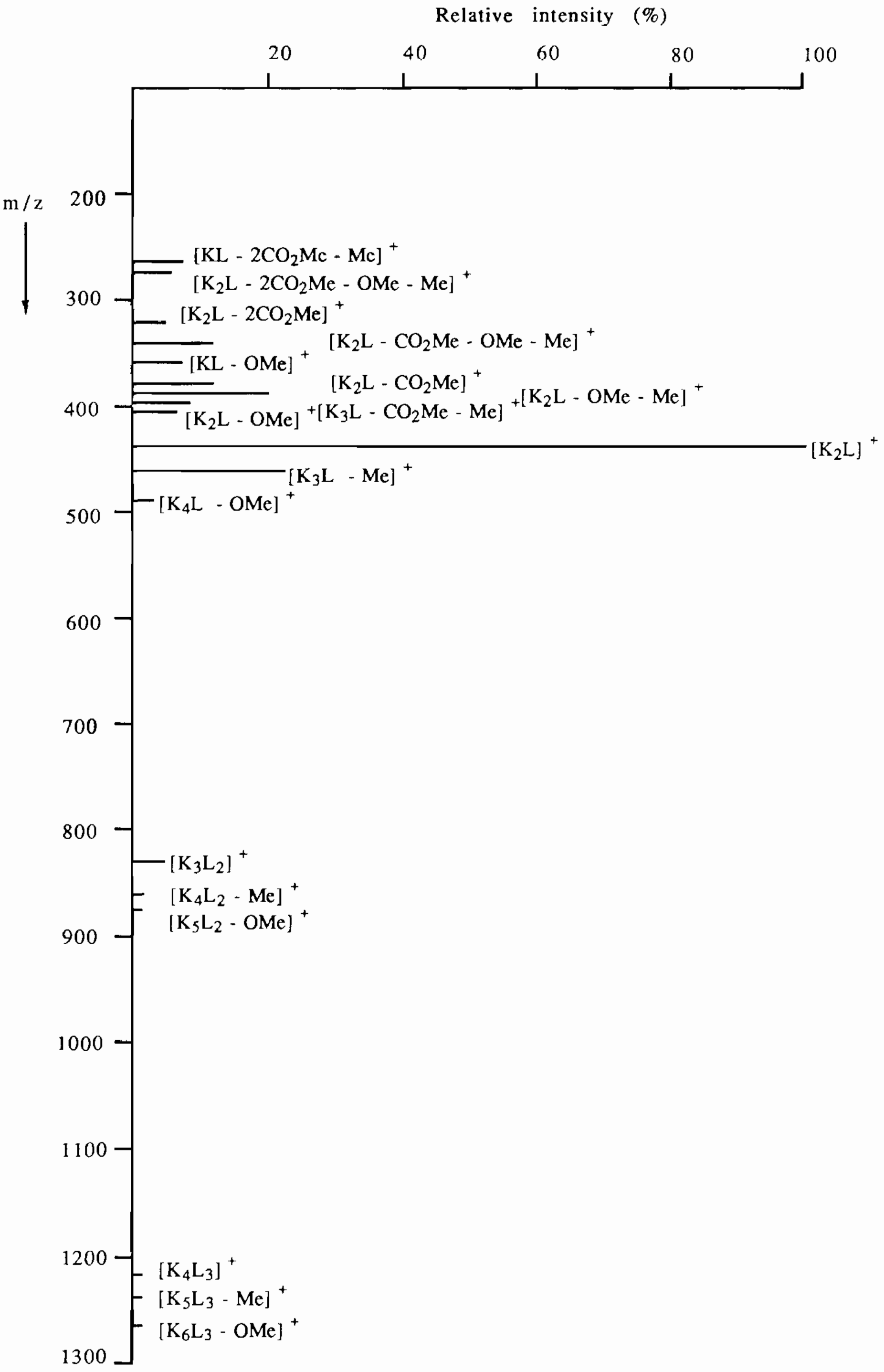


Fig. 1. Positive ion FAB mass spectrum of $K[C_5(CO_2Me)_5]$.

$[Fe(CO_2Me)(cpp)]^+$, $[Fe(OMe)(cpp)]^+$ and $[Fe(cpp)]^+$ at *m/z* 460, 442 and 411, respectively. The latter is the base peak, from which the only further loss observed is of one OMe group.

Our studies of the chemistry of $HC_5(CO_2Me)_5$ [15] resulted, *inter alia*, in the synthesis of the first mixed metallocene containing the $C_5(CO_2Me)_5$ ligand, namely $Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}$ (**2**) [16]. We have been able to compare the EI and FAB mass spectra of **2** (Table 3). Ionic compositions have been confirmed by high resolution studies carried out on the EI spectra; we assume that ions present in the FAB spectrum and

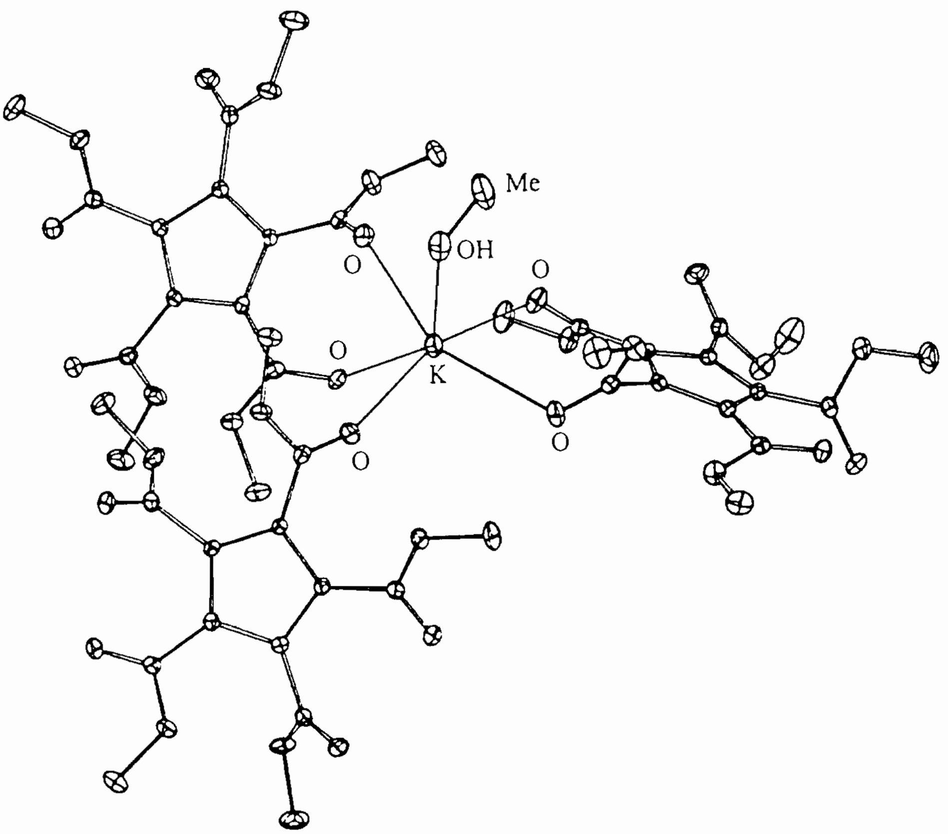
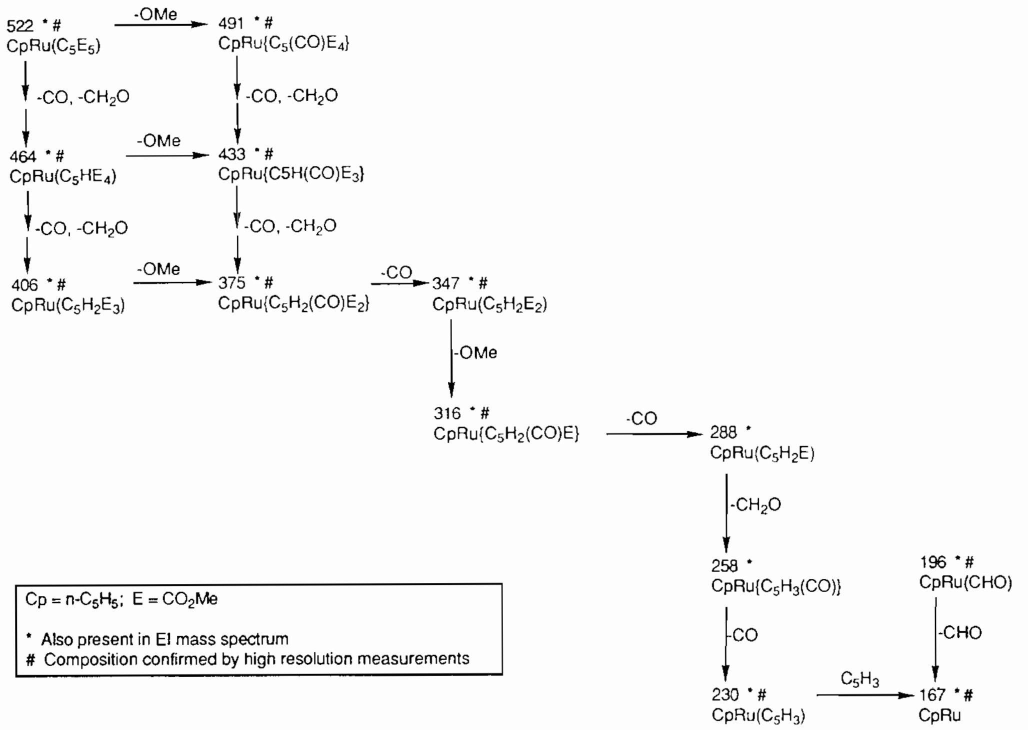


Fig. 2. X-ray structure of $K[C_5(CO_2Me)_5](MeOH)$, showing coordination about K (reproduced with permission from ref. 10).

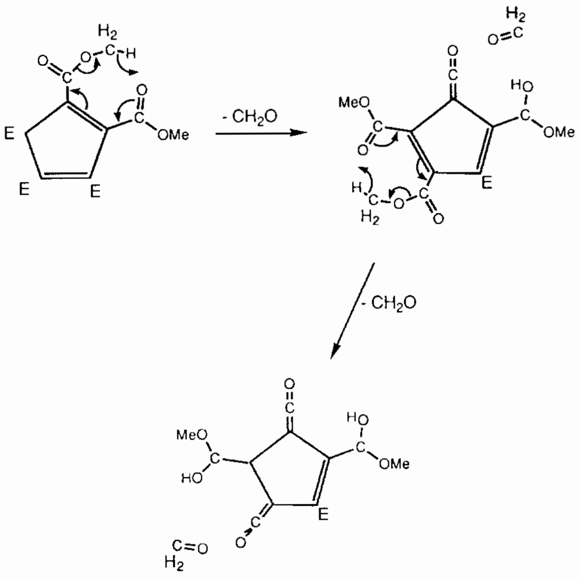
TABLE 3. FAB mass spectra of some compounds containing $C_5(CO_2Me)_5$ ligands

Positive ion	
$Fe(cpp)_2$	766, $[M]^+$, 22; 735, $[M-OMe]^+$, 86; 720, $[M-OMe-Me]^+$, 13; 704, $[M-2OMe]^+$, 8; 689, $[M-2OMe-Me]^+$, 5; 676, $[M-CO_2Me-OMe]^+$, 11; 661, $[M-CO_2Me-OMe-Me]^+$, 9; 645, $[M-CO_2Me-2OMe]^+$, 11; 589, $[M-3CO_2Me]^+$, 18; 530, $[M-4CO_2Me]^+$, 14; 470, $[Fe(CO_2Me)(cpp)]^+$, 36; 442, $[Fe(OMe)(cpp)]^+$, 32; 411, $[Fe(cpp)]^+$, 100.
$Ru(cpp)(\eta\text{-}C_5H_5)$	522, $[M]^+$, 48; 507, $[M-Me]^+$, 4; 491, $[M-OMe]^+$, 100; 477, $[M-OMe-Me]^+$, 6; 464, $[M-CO-CH_2O]^+$, 8; 433, $[M-CO_2Me-CH_2O]^+$, 9; 406, $[M-2CO-2CH_2O]^+$, 4; 375, $[M-CO_2Me-CO-2CH_2O]^+$, 8; 347, $[M-CO_2Me-2CO-2CH_2O]^+$, 7; 316, $[M-2CO_2Me-CO-2CH_2O]^+$, 10; 288, $[M-2CO_2Me-2CH_2O-CO]^+$, 14; 258, $[M-2CO_2Me-CO-CH_2O]^+$, 11; 230, $[Ru(C_5H_3)(C_5H_5)]^+$, 15; 196, $[Ru(CHO)(C_5H_5)]^+$, 3; 167, $[Ru(C_5H_5)]^+$, 38.
	Other ions present in EI mass spectrum: 293, $[C_5(CO)_2(CO_2Me)_3]^+$; 260.5, $[M]^{2+}$; 245.5, $[M-OMe]^{2+}$; 235, $[C_5H(CO)_2(CO_2Me)_2]^+$; 205, $[C_5H_2(CO)_3(CO_2Me)]^+$; 200.5, $[M-CO_2Me-2OMe]^{2+}$; 186.5, $[M-2CO_2Me-OMe]^{2+}$; 175, $[C_5H_3(CO)_4]^+$; 147, $[C_5H_3(CO)_3]^+$; 118, $[C_5H_2(CO)_2]^+$; 59, $[CO_2Me]^+$.
$Ag(cpp)(PPh_3)$	1093, $[\{Ag(PPh_3)\}_2(cpp)]^+$, 47; 831, $[Ag_2(cpp)(PPh_3)]^+$, 100; 724, $[M]^+$, 16; 693, $[M-OMe]^+$, 26; 631, $[M-3OMe]^+$, 79; 369, $[Ag(PPh_3)]^+$, 79.
Negative ion	
$Li(cpp)$	717, $[Li(cpp)_2]^-$, 100.
$K(cpp)$	3113, $[K_7(cpp)_8]^-$, 0.5; 2719, $[K_6(cpp)_7]^-$, 0.3; 2325, $[K_5(cpp)_6]^-$, 0.5; 1932, $[K_4(cpp)_5]^-$, 1; 1537, $[K_3(cpp)_4]^-$, 2; 1143, $[K_2(cpp)_3]$, 3; 749, $[K(cpp)_2]^-$, 100.

having the same nominal masses are the same as those in the EI spectrum. The parent ion (*m/z* 522; values given for ^{102}Ru) fragments by loss of CO, CH_2O and OMe groups (Scheme 2). Other ions present in the EI mass spectrum include $[Ru(CHO)(C_5H_5)]^+$ and the doubly-charged M^{2+}, $[M-OMe]^{2+}$, $[M-2OMe-CO_2Me]^{2+}$ and $[M-OMe-2CO_2Me]^{2+}$ cations. The loss of $(CO+CH_2O)$ results in formal replacement of CO_2Me by H; this process occurs for three of the five CO_2Me groups, the other two being eliminated as $(CO+OMe)$ as expected to give the interesting ion $[Ru(C_5H_3)(C_5H_5)]^+$; loss of C_5H_3 from this gives

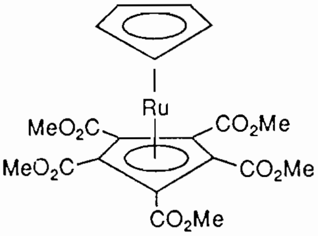


Scheme 2.



Scheme 3.

$[Ru(C_5H_5)]^+$ at *m/z* 167, which strongly supports the retention of two C_5 units in the former ion. A possible mechanism involving adjacent ester groups is shown in Scheme 3. We have recently described a related complex, $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_6H(CO_2Me)_6\}$ [17]: this compound also gives a FAB mass spectrum containing M^+ which undergoes similar elimination of $(CH_2O + CO)$ groups. In the rhodium series, this chemistry is found *in vitro* in the formation of $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2]^+$ and related chemistry [18]. The stability of the cation from



2 and eventual loss of the cpp ligand accords with the solution chemistry, where it was found that cpp can be displaced by MeCN or PR_3 (L) to give cationic $[Ru(L)_3(\eta\text{-}C_5H_5)]^+$ derivatives [16].

Experimental

Materials

The compounds $m[C_5(CO_2Me)_5]$ (m = Li, Na, K, Rb, Cs and Tl) [10], $Fe\{C_5(CO_2Me)_5\}_2$ [19], $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}$ [16] and $Ag\{C_5(CO_2Me)_5\}(PPh_3)$ [20] were made by the cited methods and were generously donated by Dr M. L. Williams.

Spectroscopy

FAB mass spectra were obtained with a VG ZAB 2HF instrument (exciting gas Ar, FAB gun voltage 7.5

kV, current 1 mA, accelerating potential 7 kV). For the ionic complexes water was used as a cosolvent and glycerol as the matrix. For most of the other complexes the cosolvent was either CH_2Cl_2 or acetone and the matrix 3-nitrobenzyl alcohol; for Ru(cpp)(η-C_5H_5) a eutectic mixture of dithiothreitol/dithioerythritol (6:1) was used. The compounds were made up as *c.* 0.5 M solutions in CH_2Cl_2 or water; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip. As the spectra frequently contained only ions of weak intensity in the high mass region, the peaks listed are restricted to the metal-containing ions that we have been able to assign. The accuracy of the spectra is of the order of ± 1 amu. Some of the spectra were obtained under maximum sensitivity/minimum resolution conditions with rapid scanning in order to record the higher mass aggregates. It is clear that there is considerable overlap in the lower mass region of the FAB mass spectra (from isotope patterns, e.g. Rb). This, combined with the usual difficulty of ion assignment in FAB mass spectrometry due to the presence of ions such as $[X+nH]^+$ or $[X-nH]^+$ associated with X^+, has meant that we have made the assignments on the basis of the most chemically reasonable formulation. We were not able to differentiate between ions that may have lost CH_2O or 2Me, and have merely indicated a possible formulation.

EI mass spectra were obtained with a GEC-Kratos MS3074 spectrometer (70 eV ionising energy, 4 kV accelerating potential).

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