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FIELD DESORPTION MASS SPECTROMETRY OF NEUTRAL π-HYDROCARBON ORGANOMETALLIC COMPLEXES

D.E. GAMES, J.L. GOWER, M. GOWER, and L.A.P. KANE-MAGUIRE

Chemistry Department, University College Cardiff, PO Box 78, Cardiff, CF1 1XL, Wales (Great Britain)

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Summary

Field desorption mass spectrometry is shown to be a useful tool for the characterisation of neutral π-hydrocarbon metal complexes. With the relatively volatile species $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) the only peaks observed are molecular, $[P]^{+\cdot}$, ions and less intense $[P + 1]^+$ and $[P + 2]^+$ ions. This contrasts with previous electron impact spectra where intensive fragmentation occurs. The field desorption mass spectra of the less volatile neutral complexes $[(\eta^6\text{-}C_6H_6)RuX_2L]$ (X = Cl, Br; L = DMSO, PPh_3) and $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, Br, I) are more complex. The base peaks in the former compounds correspond to $[P - L]^+$ ions, and further fragmentation is also apparent. No peaks corresponding to the parent dimers are seen for the $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ complexes. However, strong peaks assignable to monomeric $[(\eta^6\text{-}C_6H_6)RuX_2]$ species are observed.

Introduction

Field desorption (FD) mass spectrometry has recently been shown [1,2] to provide a novel means for the identification of salts of both classical and organometallic complexes.

This paper reports analogous studies on neutral organometallic complexes of the type $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W), $[(\eta^6\text{-}C_6H_6)RuX_2L]$ (X = Cl, Br; L = DMSO, PPh_3), and $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, Br, I). The utility of FD mass spectrometry in characterising such compounds is clearly established. In some cases comparison with electron impact (EI) mass spectra is possible, revealing marked differences in fragmentation behaviour.

Experimental

Materials

The complexes $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) were prepared by published methods [3—5] and purified by recrystallisation (Cr, Mo) from petroleum spirit (60—80°C) or sublimation (W) at 60°C and 0.05 torr pressure. Their IR spectra and melting points agreed with published data. (Found: C, 52.1; H, 3.4. $C_{10}H_8CrO_3$ calcd.: C, 52.7; H, 3.5%. Found: C, 44.0; H, 2.9. $C_{10}H_8MoO_3$ Calcd.: C, 44.2; H, 3.0%. Found: C, 33.2; H, 2.4%. $C_{10}H_8WO_3$ Calcd.: C, 33.3; H, 2.2%).

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was synthesised by the method of Zelonka and Baird [6]. The reddish-brown compound was slightly soluble in water, DMSO, and acetonitrile, but not sufficiently to permit recrystallisation. (Found: C, 29.3; H, 2.2. $C_{12}H_{12}Ru_2Cl_4$ Calcd.: C, 28.8; H, 2.4%). The related $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Br, I) were prepared by a published method [6] from the chloro complex using NaX. (Found: C, 21.4; H, 1.7; Br, 46.0. $C_{12}H_{12}Ru_2Br_4$ Calcd.: C, 21.3; H, 1.8; Br, 47.1%. Found: C, 15.9; H, 1.2; I, 53.0. $C_{12}H_{12}RuI_4$ Calcd.: C, 16.4; H, 1.4; I, 58.6%).

The compounds $[(\eta^6\text{-}C_6H_6)RuX_2L]$ (X = Cl, Br; L = PPh_3, DMSO) were prepared from the corresponding $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ dimers using published procedures [6,7]. The DMSO complexes were recrystallised from aqueous ethanol at —10°C in about 50% yield. (Found: C, 57.2; H, 4.5; Cl, 13.5. $C_{24}H_{21}PRuCl_2$ Calcd.: C, 56.3; H, 4.1, Cl, 13.9%. Found: C, 29.6; H, 3.7; Cl, 23.0. $C_8H_{12}RuCl_2SO$ Calcd.: C, 29.3; H, 3.7; Cl, 21.7%. Found: C, 23.0; H, 2.8; Br, 40.4. $C_8H_{12}RuBr_2SO$ Calcd.: C, 23.0; H, 2.9; Br, 38.4%). The X = Br, L = PPh_3 complex gave unsatisfactory analyses.

Spectroscopic measurements

FD mass spectra were recorded using a combined FD/FI/EI source on a Varian CH5D mass spectrometer linked to a Varian Spectro System 100 data system. Acetone was employed as solvent for the complexes $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) and $[(\eta^6\text{-}C_6H_6)RuX_2(PPh_3)]$ (X = Cl, Br). DMSO was used to dissolve the dimers $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, Br, I), while water was employed for $[(\eta^6\text{-}C_6H_6)RuX_2(DMSO)]$ (X = Cl, Br). The source temperature was generally 80°C, and low emitter currents were used to desorb the samples.

Results and discussion

The FD mass spectra of the relatively volatile $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo and W) complexes are summarised in Table 1. For the chromium complex, the only peaks observed are molecular, $[P]^{+\cdot}$, ions corresponding to the known chromium isotopes. Molecular $[P]^{+\cdot}$ ions also account for most of the intense peaks observed for the analogous molybdenum and tungsten compounds, although moderate $[P + 1]^+$ peaks (commonly observed in FD spectra) are also apparent, e.g. peaks at m/z 361 and 363 for $[(\eta^6\text{-}C_7H_8)W(CO)_3]$. In addition, some very weak peaks, e.g. m/z 364 in $[(\eta^6\text{-}C_7H_8)W(CO)_3]$, are assigned to $[P + 2]^+$ ions.

The most striking feature of the FD spectra of these neutral organometallic complexes is the complete absence of fragment ions. This behaviour is similar to that previously observed [1] with $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$. It is in marked contrast to the reported [8] electron impact (EI) mass spectra of $[(\eta^6\text{-}C_7H_8)M\text{-}$

TABLE 1

FIELD DESORPTION MASS SPECTRA OF [(η^6-C_7H_8)M(CO)$_3$] (M = Cr,Mo,W) COMPLEXES

Metal	Mol. wt.	m/z (% rel. int)
Cr	228	228(100), 229(17), 230(6)
Mo	274(^{98}Mo)	268(48), 270(42), 271(47), 272(55), 273(45), 274(100), 275(14), 276(29), 277(4), 278(2)
W	360(^{184}W)	358(72), 359(52), 360(83), 361(11), 362(100), 363(18), 364(3)

(CO)$_3$] species, where extensive fragmentation occurs including the stepwise loss of the three carbonyl ligands. However, it is similar to the methane chemical ionization (CI) spectra of such compounds where $[P]^{+\bullet}$ and $[P + 1]^+$ ions account for 80—90% of the sample ionization [9].

In this respect, it is interesting to note that the FD mass spectra of [π-hydrocarbon)M(CO)$_3$]BF$_4$ salts also generally show [1] prominent molecular, $[P]^{+\bullet}$, and $[P + 1]^+$ ions for the cationic part of their structure. However, in addition, ions corresponding to the loss of one CO ligand from the molecular ion are also prominent. Otherwise only minor fragmentation is generally observed with such salts. Loss of a CO ligand from these salts but not from related neutral π-hydrocarbon complexes may arise from the higher emitter currents required to desorb the former.

More complicated FD mass spectra are observed for the less volatile neutral ruthenium(II) complexes investigated here. The spectra generally varied considerably with the magnitude of the emitter current employed. Typical spectra for the [(η^6-C_6H_6)RuX$_2$(DMSO)] (X = Cl, Br) complexes are given in Table 2.

TABLE 2

FIELD DESORPTION MASS SPECTRA OF [(η-C_6H_6)RuX$_2$L] COMPLEXES (X = Cl, Br; L = DMSO, PPh$_3$)

Complex	Solvent	Molecular weight	m/z (% rel. int.)
[(η-C_6H_6)RuCl$_2$(DMSO)]	water	323Ru^{102}Cl^{35})	244(15), 246(18), 247(30), 248(35), 249(60), 250(100), 251(30), 252(98), 253(11), 254(33), 255(3), 256(6), 457(1), 458(1), 459(1.5), 460(4), 461(4), 462(4), 463(7), 464(4.5), 465(3), 466(6), 467(3), 468(2.5), 469(1.5), 470(1)
[(η-C_6H_6)RuBr$_2$(DMSO)]	water	416(Ru^{102}Br^{79})	336(24), 337(91), 338(24), 339(71), 340(100), 341(24)
[(η-C_6H_6)RuCl$_2$(PPh$_3$)]	acetone	512(Ru^{102}Cl^{35})	250(11), 251(9), 252(17), 262(100), 263(13), 509(16), 510(9), 511(6), 512(14), 513(7), 514(3), 515(12), 517(3)
[(η-C_6H_6)RuBr$_2$(PPh$_3$)]	acetone	600(Ru^{102}Br^{79})	78(100), 262(29), 334(4), 335(8), 337(11), 338(23), 340(14), 341(3), 342(25), 344(10), 590(3), 594(8), 595(14), 596(16), 597(4), 598(4), 599(16), 600(29), 601(37), 602(47), 603(22), 604(51), 605(7), 606(3)

Surprisingly, no molecular, $[P]^{+\cdot}$, peaks are seen in either case at any of the emitter currents employed. Instead, for the chloro species a base peak appears at m/z 250 corresponding to the residue (^{102}Ru ^{35}Cl) after loss of the DMSO ligand. All of the peaks between m/z 244 and 256 can be accounted for as $[P - \text{DMSO}]^+$ ions arising from the various Ru and Cl isotopes. Similarly, the analogous bromo complex shows a $[P - \text{DMSO}]^+$ peak at m/z 338 (^{102}Ru ^{79}Br) and the expected isotopic spread. These complexes are the first non-salt organometallic complexes we have encountered in which ligand loss is observed.

No further fragmentation is observed for these compounds (Table 2). However, it is noteworthy that the chloro-complex also shows a spread of peaks of low intensity corresponding to $[(\eta^6\text{-}C_6H_6)RuCl_3Ru(\eta^6\text{-}C_6H_6)]^+$ centred at m/z 465 (^{102}Ru ^{35}Cl). Combination peaks of this type were also sometimes observed [1] for organometallic salts. In the present case they may arise from the combination of two $(\eta^6\text{-}C_6H_6)RuCl_2$ fragments, with loss of a Cl ligand.

With the related $[(\eta^6\text{-}C_6H_6)RuX_2(PPh_3)]$ (X = Cl, Br) complexes, molecular, $[P]^{+\cdot}$, ions are observed centred at m/z 512 (^{102}Ru ^{35}Cl) and 600 (^{102}Ru ^{79}Br), respectively (Table 2). However, once again the fragment ions $[(\eta^6\text{-}C_6H_6)RuX_2]^+$ are also observed at m/z 250 (^{102}Ru ^{35}Cl) and 338 (^{102}Ru ^{79}Br), respectively. Loss of the PPh_3 ligand is confirmed by the appearance of a strong peak at m/z 262 in both cases (this is the base peak for the chloro compound). The base peak at m/z 78 for the bromo complex in Table 2 is assigned to benzene, indicating further fragmentation.

The FD mass spectra of the dimeric $[(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, Br, I) complexes in DMSO also reveal some interesting novel features (Table 3). No peaks corresponding to the parent dimers are seen. However, in each case strong peaks corresponding to the monomeric $(\eta^6\text{-}C_6H_6)RuX_2$ species are observed, centred at m/z 250 (^{102}Ru ^{35}Cl), 338 (^{102}Ru ^{79}Br), and 434 (^{102}Ru ^{127}I), respec-

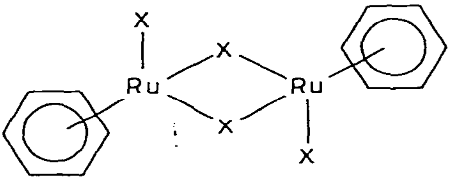
TABLE 3

FIELD DESORPTION MASS SPECTRA OF $[(\eta\text{-}C_6H_6)RuX_2]_2$ COMPLEXES (X = Cl, Br I)

Complex	Solvent	Molecular weight	m/z (% rel. int.)
$[(\eta\text{-}C_6H_6)RuCl_2]_2$	DMSO	500(Ru^{102}Cl^{35})	78(28), 80(17), 81(100), 242(0.5), 244(4), 247(5), 248(6), 249(11), 250(18), 251(7), 252(13), 253(1.5), 254(11)
$[(\eta\text{-}C_6H_6)RuBr_2]_2$	$CHCl_3$ DMSO	676(Ru^{102}Br^{79})	334(44), 340(81), 342(100), 293(4), 294(3), 295(2), 296(3), 297(1), 298(3), 300(1), 332(6), 334(14), 335(16), 336(30), 337(69), 338(66), 339(65), 340(100), 341(22), 342(69)
$[(\eta\text{-}C_6H_6)RuI_2]_2$	DMSO	868(Ru^{102})	78(28), 80(10), 81(7), 336(14), 339(9), 340(10), 341(24), 342(13), 351(19), 428(24), 430(15), 431(43), 432(71), 433(77), 434(100), 435(9), 436(82), 437(10), 733(5), 734(7), 736(15), 737(14), 738(10), 739(20), 740(13), 741(21), 742(8), 743(10), 745(8)

tively. The EI mass spectrum of the choro dimer also gives an ion at *m/z* 250 corresponding to the monomer.

The doubly-halogeno-bridged structure I has been proposed [6] for these



(I)

dimers in the solid state. It therefore appears that bridge cleavage has occurred in the mass spectrometer. Alternatively, since the dimers are known [7] to react with DMSO to give [$(\eta^6\text{-}C_6H_6)RuX_2DMSO)$], it is possible that the spectra in Table 3 are merely those of the latter monomeric complexes (see Table 2) formed while loading the samples onto the emitter surface. However, this alternative seems unlikely, since the FD mass spectrum of [$(\eta^6\text{-}C_6H_6)RuBr_2]_2$ also shows only monomeric peaks when non-nucleophilic chloroform is used as solvent (Table 3).

Interestingly, the spectrum of the iodo complex in DMSO includes a further isotopic spread centred on *m/z* 741 (^{102}Ru), which can be assigned to the complex [$(\eta^6\text{-}C_6H_6)RuI_3Ru(\eta^6\text{-}C_6H_6)$] (Table 3). This species is presumably formed in the mass spectrometer in a manner similar to the analogous chloro-complex found in trace amounts in the spectrum of [$(\eta^6\text{-}C_6H_6)RuCl_2(DMSO)$] (see above).

The peak at *m/z* 78 for [$(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, I) is due to either the DMSO solvent or a benzene fragment. However, the source of the *m/z* 80 and 81 peaks in these spectra is puzzling, but may arise from cyclohexa-1,3-diene and protonated cyclohexa-1,3-diene, respectively. Finally, the isotopic spread centred on *m/z* 294 (^{102}Ru ^{35}Cl ^{79}Br) found in the spectrum of the X = Br dimer in DMSO corresponds to [$(\eta^6\text{-}C_6H_6)RuClBr$], indicating the presence of a trace impurity in the sample.

In conclusion, the above results confirm the utility of FD mass spectrometry as a tool for rapid identification of neutral π-hydrocarbon metal complexes. With relatively volatile species such as [$(\eta^6\text{-triene})M(CO)_3$] (M = Cr, Mo, W) little or no fragmentation is observed, and molecular, $[P]^{+\cdot}$, ions account for all or most of the intense peaks. Our similar experience [10,11] with related [$(\eta^4\text{-diene})M(CO)_3$] (M = Fe, Os) compounds suggests that this simple behaviour may be common to the majority of relatively volatile π-hydrocarbon metal complexes. In contrast, with less volatile neutral compounds such as the [$(\eta^6\text{-}C_6H_6)RuX_2L$] (X = Cl, Br; L = DMSO, PPh$_3$) and [$(\eta^6\text{-}C_6H_6)RuX_2]_2$ (X = Cl, Br, I) studied here, significant fragmentation occurs and in many cases no parent molecular ions are observed.

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