Journal of Organometallic Chemistry, 88 (1975) 345—349
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

FIELD DESORPTION MASS SPECTROMETRY OF ORGANOMETALLIC COMPLEX SALTS

D.E. GAMES, A.H. JACKSON, L.A.P. KANE-MAGUIRE AND K. TAYLOR
Department of Chemistry, University College Cardiff, P.O. Box 78, Cardiff, CF1 1XL (Great Britain)

(Received October 28th, 1974)

Summary

The field desorption spectra of $[(L)M(CO)_3]^+BF_4^-$ [M = Fe, L = cyclo-C_6H_7, cyclo-C_7H_9, cyclo-$C_{10}H_{11}$, 2-MeO-cyclo-C_6H_7; M = W, L = cyclo-C_7H_7], $[(Ar)Fe(C_5H_5)]^+PF_6^-$ [Ar = C_6H_6, $CH_3C_6H_5$, $(CH_3)_3C_6H_3$], $[(cyclo\text{-}C_8H_{11})Co(C_5H_5)]^+BF_4^-$ and $[(C_6H_6)Cr(CO)_3]$ have been obtained. In all cases molecular or quasi-molecular ions for the cations were present, usually as the base peaks in the spectra. Fragment ions corresponding to metal—ligand cleavages were also found in most cases.

Introduction

The mass spectral study of salt-like organometallic complexes is difficult because they do not readily volatilize under electron impact conditions. Hence compounds of this type are normally identified by the mass spectra of their pyrolysis products [1]. Since field desorption (FD) mass spectrometry enables mass spectra to be obtained from compounds which are labile and/or have low volatility [2], we have examined the utility of the technique for the characterization of organometallic complex salts. The FD spectra of the following salts were studied: $[(L)M(CO)_3]^+BF_4^-$ [L = cyclohexadienyl, M = Fe (compound I); L = cycloheptadienyl, M = Fe (II); L = benzocyclohexadienyl, M = Fe (III); L = 2-methoxycyclohexadienyl, M = Fe (IV); L = tropylium, M = W (V)], [(arene)-Fe(cyclopentadienyl)]$^+PF_6^-$ [arene = benzene (VII), toluene (VIII), and mesitylene (IX)], and [(2,5-cyclooctadienyl)Co(cyclopentadienyl)]$^+BF_4^-$ (X). An FD spectrum of the neutral complex tricarbonyl(benzene)chromium (VI) was also recorded. The electron impact (EI) and chemical ionization (CI) spectra of this latter compound have both been reported [3,4], and its FD spectrum was obtained for comparison with the spectra obtained by these other methods.

TABLE 1

FIELD DESORPTION SPECTRA OF TRICARBONYL(π-HYDROCARBON) ORGANOMETALLIC COMPLEXES

No.	Complex	Mol. wt. of cation	m/e (% rel. int.)
I	$[(C_6H_7)Fe(CO)_3]^+BF_4^-$	219	78(44) 79(64) 189(7) 191(100) 192(12) 218(8) 219(36) 220(81)
II	$[(C_7H_9)Fe(CO)_3]^+BF_4^-$	233	93(12) 112(4) 191(3) 202(4) 203(4) 204(100) 205(58) 206(9) 219(8) 231(7) 232(7) 233(54) 234(13) 235(1)
III	$[(C_{10}H_{11})Fe(CO)_3]^+BF_4^-$	271	128(4) 130(36) 242(18) 243(15) 269(26) 270(46) 271(100) 272(33) 273(5)
IV	$[(C_6H_6OMe)Fe(CO)_3]^+BF_4^-$	249	108(19) 196(8) 219(6) 220(13) 221(29) 222(11) 247(6) 248(7) 249(80) 250(100) 251(16) 252(3) 442(9) 443(3)
V	$[(C_7H_7)W(CO)_3]^+BF_4^-$	357	91(1) 311(25) 312(21) 313(26) 314(2) 315(29) 329(6) 330(4) 331(6) 332(2) 333(7) 348(12) 349(6) 350(13) 351(1) 352(14) 357(84) 358(55) 359(100) 360(13) 361(86) 362(15) 363(1)
VI	$[(C_6H_6)Cr(CO)_3]$	214	212(5) 214(100) 215(20) 216(7)

Experimental

The tricarbonyl(π-hydrocarbon)metal tetrafluoroborates I-V and the cyclopentadienyl(π-hydrocarbon)metal salts VII-X were prepared by previously reported methods [5-9].

Field desorption spectra were obtained using a Varian combined FD/FI/EI source on a CH5D mass spectrometer linked to a Varian 620i data system. The data system was calibrated in the EI mode using PFK. Acetone was used as a solvent in all cases, the source temperature was 80° and emitter currents of 10-13 mA were used to desorb the sample. Desorption of sample was very rapid in some cases and not smooth in others; hence for these compounds variations in the relative intensities of ions were observed in spectra obtained from separate runs of the same sample. However, the same ions were always present in spectra taken under similar conditions.

Results and discussion

The FD spectra obtained from the tricarbonyl(π-hydrocarbon) organometallic salts I-V are summarised in Table 1. All the compounds had prominent molecular, P^+, and $[P+1]^+$ ions for the cationic part of their structure in their spectra. The $[P+1]^+$ ions were readily identifiable since their intensity relative to the P^+ ions decreased at higher emitter currents. Ions corresponding to loss of one CO from the molecular ion were common to all the spectra. This feature is similar to the breakdown behaviour observed in the EI mass spectra of neutral tricarbonyl(π-hydrocarbon)metal complexes [1]. However, unlike the EI studies, no peaks were observed for the stepwise loss of further carbonyl groups. The FD spectra of the salts III and IV had ions at *m/e* 130 and 108 respectively corresponding to [π-hydrocarbon ligand $-1]^+$. In contrast, ions corresponding to [π-hydrocarbon ligand$]^+$ were present in the spectra of the salts II and V, and salt I had ions corresponding to both types of behaviour in its spectrum. Two groups of ions at *m/e* 311 and 348 are present in the spectrum of tricarbonyl(tropylium)tungsten tetrafluoroborate (V). Both are consistent with the presence of tungsten in them, but we are unable to find any rational explanation for them and can only conclude that they are due to impurities present in the sample.

P^+ ions are the base peaks in the FD spectra of all the cyclopentadienyl(arene)metal salts VII-X (Table 2). Also, at higher emitter currents ions are present in the iron complexes which correspond to π-hydrocarbon and cyclopentadiene ligands. All the compounds show an ion at *m/e* 186 for the iron complexes and *m/e* 189 for the cobalt complex X which correspond to the formation of ferrocenyl or cobaltocenyl ions. Since the cleavages necessary to form these ions appear unlikely, the possibility that they arise from impurities present in the salts was considered. However, a further recrystallisation of salt IX from water did not significantly alter its FD spectrum. The most likely explanation for the presence of these dicyclopentadienylmetal ions is that they are produced by thermal decomposition of the compounds during their introduction into the mass spectrometer. Similar appearances of dicyclopentadienylmetal ions have been reported in the EI spectra of a variety of neutral

TABLE 2

FIELD DESORPTION SPECTRA OF CYCLOPENTADIENYL(π-HYDROCARBON) ORGANOMETALLIC SALTS

	Complex	Mol. wt. of cation	*m/e* (% rel. int.)
VII	$[(C_6H_6)Fe(C_5H_5)]^+PF_6^-$	199	186(10) 197(14) 199(100) 200(24) 201(2) 543(4) [a]65(1) 78(2) 184(2) 186(55) 187(7) 188(2) 197(8) 198(1) 199(100) 200(14) 543(4)
VIII	$[(C_6H_5CH_3)Fe(C_5H_5)]^+PF_6^-$	213	213(100) 214(29) [a]92(9) 186(4) 211(10) 213(100) 214(15) 215(2) [a]65(10) 69(2) 92(37) 93(2) 107(3) 184(3) 186(60) 187(7) 211(4) 213(100) 214(23)
IX	$[(C_6H_3(CH_3)_3)Fe(C_5H_5)]^+PF_6^-$	241	239(5) 241(100) 242(17) 243(1) [a]65(1) 69(2) 120(10) 186(2) 239(8) 240(1) 241(100) 242(17) 243(1)
X	$[(C_8H_{11})Co(C_5H_5)]^+BF_4^-$	231	189(21) 190(4) 229(68) 230(10) 231(100) 232(13) [a]189(100) 190(27) 203(2) 229(80) 230(14) 231(13) 464(24) 504(18) 544(5)

[a] Higher wire currents.

complexes of the type [$RFe(CO)_2(C_5H_5)$] [9].

Cluster ion formation was observed in the spectra of iron salt VII, the ion at *m/e* 543 corresponding to a composition [$\{(C_6H_6)Fe(C_5H_5)\}_2PF_6]^+$. The cobalt salt X also had abundant ions at *m/e* 544, 504 and 464 in its spectrum at higher wire currents. At present we are unable to ascertain with complete certainty whether these ions are cluster ions from the salt, or are due to impurities in the sample. However, on the basis of our current evidence the latter explanation is favoured.

The FD spectrum of tricarbonyl(benzene)chromium consists only of a molecular ion; no fragment ions were observed either in the FD or the FI spectrum of this compound. This behaviour contrasts with that observed in electron impact where extensive fragmentation is observed [3], but is similar to the methane CI spectrum [4] where $[P]^+$ and $[P+1]^+$ ions accounted for 80-90% of the sample ionization.

The above mass spectra are believed to be the first obtained for organometallic complex salts. They show that field desorption mass spectrometry is indeed a useful tool for the characterization of such salts. The relatively mild conditions involved result in less fragmentation than in EI techniques, and a fairly ready identification of the ligands present in the complex.

Acknowledgements

We thank the S.R.C. and the Royal Society for financial assistance in the purchase of the mass spectrometer and the combined FD/FI/EI source, and one of us (K.T.T.) thanks the S.R.C. for financial support.

References

1 J. Müller, Angew Chem., 11 (1972) 653.
2 H.-R. Schulten, H.D. Beckey, G. Eckhardt and S.H. Doss, Tetrahedron, 29 (1973) 3861 and refs. therein.
3 J. Müller and K. Fenderl, Chem. Ber., 103 (1970) 3128.
4 W.P. Anderson, N. Hsu, C.W. Stanger, Jr. and B. Munson, J. Organometal. Chem., 69 (1974) 249.
5 A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, J. Chem. Soc. A, (1968) 332.
6 M.A. Hashmi, J.D. Munro and P.L. Pauson, J. Chem. Soc. A, (1967) 240.
7 J.D. Munro and P.L. Pauson, Proc. Chem. Soc., (1959) 267.
8 I.U. Khand, P.L. Pauson and W.E. Watts, J. Chem. Soc. C, (1968) 2257.
9 J. Lewis and A.W. Parkins, J. Chem. Soc. A, (1967) 1150.
10 R.B. King, J. Amer. Chem. Soc., 90 (1968) 1417.