

Electrospray mass spectrometric studies of some heterometal anionic carbonyl clusters

Montserrat Ferrer, Roser Reina, Oriol Rossell, Miquel Seco^{*}, Glòria Segalés

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Received 19 October 1995

Abstract

Electrospray mass spectra (ESMS) are reported for a series of anionic transition-metal clusters of the type $(\text{PPh}_4)[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-Hg}(m)\}]^-$ ($m = \text{Mo}(\text{CO})_3\text{Cp}$; $\text{Co}(\text{CO})_4$; $\text{Fe}(\text{CO})_2\text{Cp}$; $\text{W}(\text{CO})_3\text{Cp}$; $\text{Mn}(\text{CO})_5$) and also for the species of higher nuclearity $(\text{NEt}_4)[\text{Fe}_6\text{C}(\text{CO})_{16}\text{AuPPh}_3]$ in methanol solution. The results were compared with those obtained by FAB-MS, and they indicate that ESMS is the most appropriate technique by which to obtain control fragmentation. Information about the strength of the different metal–metal bonds present in the cluster can be deduced from the species generated.

Keywords: Electrospray mass spectroscopy; Carbonyl clusters; Metal–metal bonds

1. Introduction

In the last few years the use of new techniques of ionization in mass spectrometry has made possible the characterization of a wide range of coordination compounds and organometallic complexes. Classical techniques such as electron impact (EI) or chemical ionization (CI) usually lead to extensive fragmentation and no molecular ion is detected. Then, many efforts have been made to develop softer ionization techniques like plasma desorption (PD), laser desorption (LD), secondary ionization mass spectrometry (SIMS), fast atom bombardment (FAB) or electrospray mass spectrometry (ESMS). The last technique is of particular interest for the characterization of very labile compounds, since it causes minimum fragmentation of the molecule. Although this technique has been applied in the characterization of large biomolecules [1], it has recently been used successfully to investigate solutions of inorganic and organometallic compounds. It appears to be a particularly useful way to study inorganic species for which multinuclear NMR is unavailable [2].

These results prompted us to use this technique in the study of heterometal transition cluster anions. The characterization of such compounds has been a major prob-

lem in this area and generally requires the use of single-crystal X-ray crystallography. The lability of such species, along with their thermal instability and the easy cleavage of metal–metal bonds, means that the method of transferring pre-existing ions from solution to the gas phase used in ESMS is the best, since it causes minimal fragmentation of the molecule. Also, there are no special requirements in sample preparation and the only condition is that the compound must be soluble (and stable) in a suitable solvent, and this technique is extremely easy to use.

Here we report the FAB-MS and ESMS of a series of heterotransition-metal anionic clusters $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-Hg}(m)\}]^-$ ($m = \text{Mo}(\text{CO})_3\text{Cp}$ (1); $\text{Co}(\text{CO})_4$ (2); $\text{Fe}(\text{CO})_2\text{Cp}$ (3); $\text{W}(\text{CO})_3\text{Cp}$ (4); $\text{Mn}(\text{CO})_5$ (5)). The data obtained by both techniques are compared and ESMS is shown to be the most appropriate method to study ionic cluster compounds.

2. FAB-MS

Hitherto, FAB-MS has been the most widely used technique to obtain spectral data for metal-containing complexes which are thermally labile or unstable in conventional EI or CI mass spectrometry. Table 1 lists the m/z values of the strongest peak in the isotopic mass distribution and relative intensities (100 as the

^{*} Corresponding author.

Table 1
FAB-MS and ESMS data for the complexes (PPh₄)[Fe₃(CO)₁₀(μ-CO)(μ-Hg(m))] (m = Mo(CO)₃Cp (1); Co(CO)₄ (2); Fe(CO)₂Cp (3); W(CO)₃Cp (4); Mn(CO)₅ (5))

Fragment	FAB(-) ^c Electropray ^d			FAB(-) ^c Electropray ^d			FAB(-) ^c Electropray ^d		
	SV = 50	SV = 55	SV = 70	SV = 50	SV = 55	SV = 70	SV = 50	SV = 55	SV = 70
	<i>m</i> = Mo(CO) ₃ Cp (1)			<i>m</i> = Co(CO) ₄ (2) ^a			<i>m</i> = Fe(CO) ₂ Cp (3)		
M ⁻	921(13)	43	—	849(32)	26	13	—	—	—
M-CO ⁻	893(23)	100	10	821(63)	100	100	—	—	—
M-2CO ⁻	865(10)	20	14	793(22)	24	44	3	5	—
M-3CO ⁻	837(40)	15	100	764(44)	18	55	4	23	8
M-Hg-4CO ⁻	608(30)	—	2	535(100)	6	13	16	30	100
M-Hg-5CO ⁻	580(3)	—	—	507(16)	—	—	2	—	—
M-Hg-6CO ⁻	552(5)	—	—	479(51)	—	—	3	—	—
M-Hg-7CO ⁻	524(16)	—	—	451(50)	—	—	8	—	—
M-Hg-8CO ⁻	496(3)	—	—	423	—	—	1	—	—
A ⁻	476(33)	—	—	476(51)	—	—	40	—	—
A-CO ⁻	448(60)	—	—	448(50)	—	—	—	—	—
A-2CO ⁻	420(71)	—	—	420(54)	—	—	—	—	—
A-3CO ⁻	392(100)	—	—	392(84)	—	—	—	—	—
A-4CO ⁻	364(38)	—	—	364(31)	—	—	—	—	—
A-5CO ⁻	336(43)	—	—	336(30)	—	—	—	—	—
	<i>m</i> = W(CO) ₃ Cp (4) ^b			<i>m</i> = Mn(CO) ₅ (5)			<i>m</i> = Fe(CO) ₂ Cp (3)		
M ⁻	1009(32)	39	—	873(26)	27	14	—	—	—
M-CO ⁻	981(46)	100	9	845(63)	100	100	8	—	—
M-2CO ⁻	953(19)	19	12	817(17)	18	28	7	—	—
M-3CO ⁻	925(79)	17	65	789(100)	35	92	100	—	—
M-Hg-4CO ⁻	696(38)	—	—	560(36)	—	5	54	1	—
M-Hg-5CO ⁻	668(8)	—	—	532(32)	—	—	31	3	—
M-Hg-6CO ⁻	641(16)	—	—	504(16)	—	—	9	2	—
M-Hg-7CO ⁻	612(33)	—	—	—	—	—	—	—	—
M-Hg-8CO ⁻	584(10)	—	—	—	—	—	—	—	—
A ⁻	476(42)	—	—	—	—	—	—	—	—
A-CO ⁻	448(68)	—	—	476(97)	—	—	12	47	—
A-2CO ⁻	420(76)	—	—	448(66)	—	—	—	100	—
A-3CO ⁻	392(100)	—	—	420(58)	—	—	—	7	—
A-4CO ⁻	364(32)	—	—	392(85)	—	—	2	2	—
A-5CO ⁻	336(59)	—	—	364(38)	—	—	2	1	—
				336(37)	—	—	—	1	—

SV = skimmer voltage.

Peaks with intensity lower than 1% not included.

Additional peaks: ^a M-4CO, FABS 563(53); intensity in ESMS at different SV; 11, 22, 34, —; M-Hg-9CO, FABS 395(43); intensity in ESMS at 100 SV; 11. ^b M-6CO, FABS 842(1); M-7CO, FABS 814(4); M-Hg-9CO, FABS 556(33); intensity in ESMS at 100 SV; 2; M-Hg-10CO, FABS 528(4).

^c Intensity in parentheses.

^d Intensity of observed peaks at different skimmer voltages.

maximum) of the fragment ions observed for each of the transition-metal clusters studied in FAB-MS. All spectra were obtained using NBA as the matrix. The spectrum obtained for $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-HgMn}(\text{CO})_5\}]^-$ (**5**) is shown in Fig. 1 and can be considered representative. Characteristic molecular weight information was observed for each cluster, although the relative abundances of the molecular ions were, in general, less than 30%. Although in the literature additional peaks due to (i) adducts with the matrix, (ii) peaks corresponding to the addition of matrix atoms, or (iii) substitution of ligands by the matrix under fast atom bombardment conditions, have often been observed [3], we did not detect the occurrence of any of these processes in this study. As can be seen in the data summarized in Table 1, FAB-MS of **1–5** afforded abundant ion cluster fragments. The ionization mode in FAB-MS shows a fragmentation pattern of the anion (M^-) due to a sequential loss of CO. In most cases, the peak corresponding to $|\text{M}-n\text{CO}|^-$ ($n = 1, 2, 3$) anions has a relatively high intensity (e.g. $|\text{M}-3\text{CO}|^-$ 79% for **4**). This fact suggests that the loss of the first CO ligands can occur in (or near) the matrix, as described for the heptaosmium hydrido clusters $[\text{H}_2\text{Os}_7(\text{CO})_n]^-$ ($n = 20, 21, 22$) [4]. We

were not able to observe the naked Fe_3Hgm anion in any case. Presumably, the soft ionization conditions associated with FAB-MS preclude the ejection of all CO ligands, because the loss of each carbonyl ligand makes the cluster more electron deficient and increases the strength of both M–M and M–L bonds.

An interesting feature of all FAB-MS spectra is the existence of ions corresponding to fragmentation of the metal skeleton. The geometry of these pentametallic clusters consists of a spiked butterfly metal arrangement (Fig. 1). If we compare the data obtained for all compounds, we can observe one peak at $m/z = 476$ which is attributable to the species $|\text{M}-\text{HgM}|^-$ (A^-). This fact can be understood as the dissociation of the Hgm unit to produce the cluster anion $[\text{Fe}_3(\text{CO})_{11}]^-$. These results correlate well with the chemistry of $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-Hg(m)}\}]^-$ since these clusters are obtained in solution by the reaction of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ and ClHgM [5]. Although the $|\text{A}^-|$ anion was characterized by EPR some years ago [6], its isolation and definitive characterization by X-ray diffraction studies has been reported only recently [7]. The existence of these radical anions suggests an important role for one-electron pathways in the chemistry of iron carbonyl

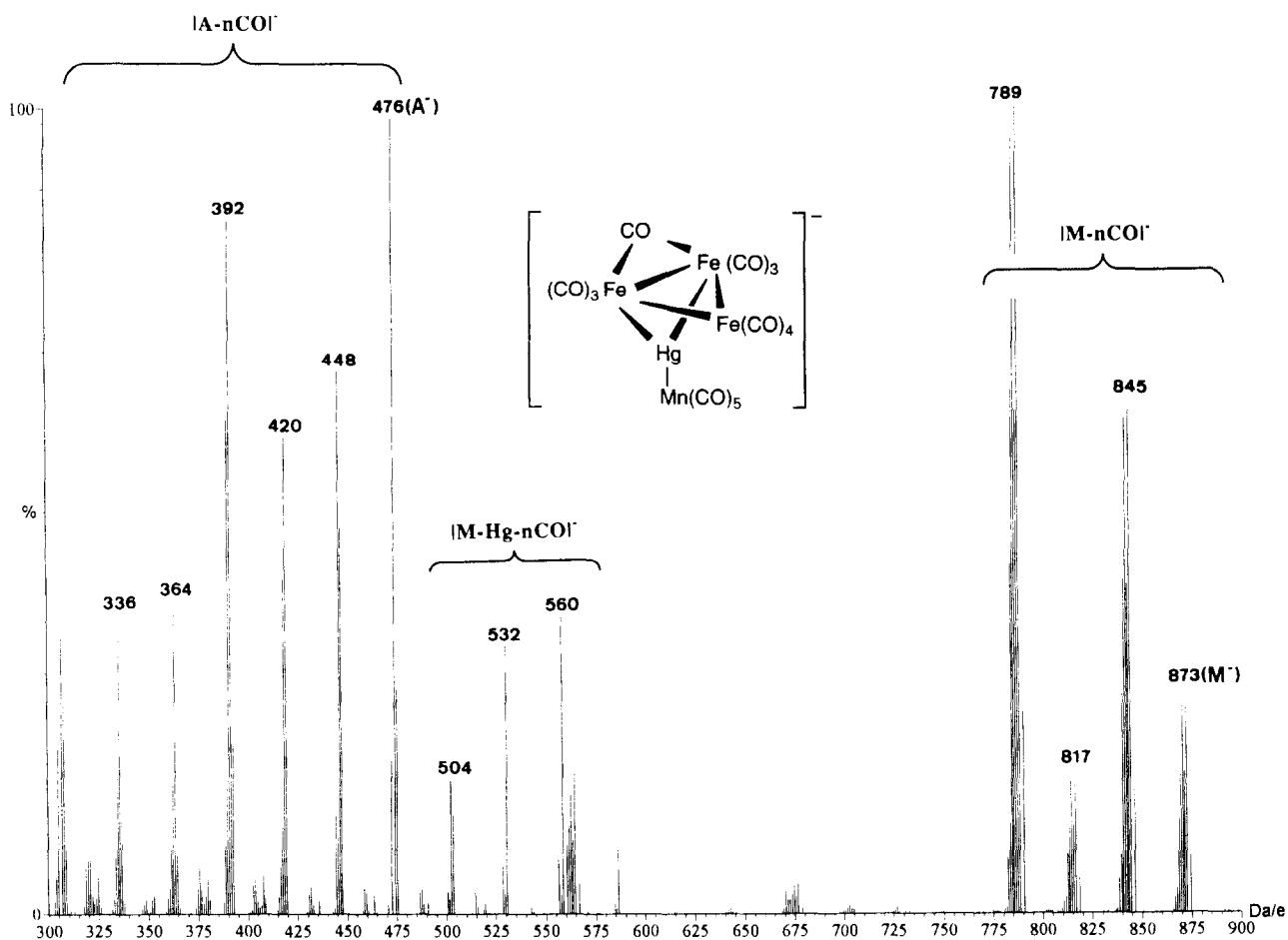


Fig. 1. FAB-MS spectrum of $(\text{PPh}_4)[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-HgMn}(\text{CO})_5\}]^-$ (**5**).

compounds. Thus, $|\mathbf{A}^-|$ has been invoked as a key intermediate in the electron-transfer catalyzed substitution reactions of $\text{Fe}_3(\text{CO})_{12}$ [8].

Additionally, we observed the degradation of $|\mathbf{A}^-|$ by loss of five carbonyl ligands at the most. Interestingly, the species corresponding to the loss of three CO ligands, $|\mathbf{A}-3\text{CO}^-|$, is the most abundant in all spectra according to the intensity peak values.

However, peaks due to the $|\mathbf{M}-\text{Hg}(\text{CO})_n^-|$ species were observed in all cases. The presence of these ions in the FAB-MS spectra can be understood as a demercuration process of the parent anion, giving the corresponding $[\text{Fe}_3(\text{CO})_{11}(\text{m})]^-$ anions. Demercuration reactions have been widely observed in transition-mercury clusters by both thermic and photochemical processes, giving the product corresponding to the coupling of the two groups attached to the mercury atom [9]. These new species generate new anions resulting from sequential loss of from four to nine CO ligands, depending on the m fragment present in the parent ion.

3. ESMS

The ES mass spectra obtained for each of the transition-metal cluster anions at different skimmer voltages (50, 55, 70 and 100 V) are summarized in Table 1. The spectra obtained for $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-HgMn}(\text{CO})_5\}]^-$ (**5**) are shown in Fig. 2. In all cases the experimental isotopic mass distributions agree with the calculated pattern and no peaks for m/z ($z > 1$) were observed. At relatively low skimmer voltages (50 V) the spectra are dominated by the peak corresponding to $|\mathbf{M}-\text{CO}^-|$ species, but those due to the intact molecular ion of the corresponding substance are intense. When the skimmer voltage was increased to 55 V, the peak due to the $|\mathbf{M}-\text{CO}^-|$ anion still had the highest intensity, although that of the molecular ion was lower in all cases. An increase in the intensity of the peaks corresponding to $|\mathbf{M}-n\text{CO}^-|$ was observed.

Interestingly, skimmer voltages of 70 V produced drastic changes in the spectrum of these compounds. Thus, the signal of the molecular anion disappeared and the peaks due to the demercurated species $|\mathbf{M}-\text{Hg}-n\text{CO}^-|$ emerged with an intensity from 25 to 100 depending on the m fragment. These data reflect the relative thermodynamic stability of the Fe_3HgM arrays and agree with the strength of the metal–metal bonds in these arrangements. We observed that the intensities of the $|\mathbf{M}-\text{Hg}-4\text{CO}^-|$ peak decreased in the sequence $\text{Co} > \text{Mn} > \text{Mo} > \text{W} > \text{Fe}$ according to the increase of nucleophilicity of the anions. Bearing in mind that the $[\text{Co}(\text{CO})_4]^-$ fragment is the lowest nucleophile [10], this sequence is in good accord with the easier demercuration process detected in the cobalt complex. Alternatively, it is worth noting that only in the case of $\mathbf{3}^-$

(containing the highest nucleophile $\text{Fe}(\text{CO})_2\text{Cp}$ group) were no peaks corresponding to $|\mathbf{M}-\text{Hg}-n\text{CO}^-|$ fragments observed, confirming the strength of the Fe–Hg bond. Moreover, these results agree with that obtained in the redox study of these complexes, where $\mathbf{3}^-$ was the most easily oxidable compound [5].

When the skimmer voltage used was 100 V no peaks due to $|\mathbf{M}-n\text{CO}^-|$ were observed in the spectra, except for $\mathbf{3}^-$ where the peak corresponding to $|\mathbf{M}-3\text{CO}^-|$ appeared, being in this case the signal of greatest intensity. This corroborates the observations at 70 V, showing that the Fe_3HgFe array is the strongest. Interestingly, no signals due to the $|\mathbf{M}-\text{Hg}-n\text{CO}^-|$ species in the spectrum of $\mathbf{3}^-$ were observed. Consequently, we can conclude that $|\mathbf{A}^-|$ anions must be obtained directly by scission from the molecular species, and that the $|\mathbf{M}-\text{Hg}-n\text{CO}^-|$ anions are not involved in this mechanism.

We have been able to extend the good results obtained in the characterization of these anion clusters by ESMS to the species $(\text{NEt}_4)[\text{Fe}_6\text{C}(\text{CO})_{16}\text{AuPPh}_3]^-$, which shows higher nuclearity, lability and instability. When $[\text{Fe}_6\text{C}(\text{CO})_{16}\text{AuPPh}_3]^-$ [11] was treated under FABS conditions a high number of peaks due to loss of carbonyls and metal core breaking could be observed (Fig. 3). In this case the peak due to the parent ion was much lower than that attributable to the other species generated. In contrast, the ESMS spectrum at skimmer voltage 50 V shows only two major peaks, the most intense attributable to the parent ion and the second corresponding to the loss of one carbonyl ligand.

It is remarkable that both in this spectrum and in those corresponding to $(\text{PPh}_4)[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-Hg}(\text{m})\}]^-$ complexes, all signals observed in each ESMS spectrum can be seen in the corresponding FAB-MS spectrum, the most striking difference between them being the specificity of the species generated with different skimmer voltage in the mass spectra obtained by ESMS. These results indicate that ESMS, being a softer ionization technique than FAB-MS for the study of heterometal-cluster ions, provides a method to generate or characterize charged species that are difficult to synthesize or detect by other techniques.

4. Experimental section

The metal cluster anions $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})\{\mu\text{-Hg}(\text{m})\}]^-$ ($\text{m} = \text{Mo}(\text{CO})_3\text{Cp}$ (**1**); $\text{Co}(\text{CO})_4$ (**2**); $\text{Fe}(\text{CO})_2\text{Cp}$ (**3**); $\text{W}(\text{CO})_3\text{Cp}$ (**4**); $\text{Mn}(\text{CO})_5$ (**5**)) were obtained as PPh_4^+ salts by reaction of $(\text{PPh}_4)_2-[\text{Fe}_3(\text{CO})_{11}]$ with ClHgM in THF at -15°C [5]. Electrospray mass spectra were recorded at Servei de Espectroscopia de Masses de la Universitat de Barcelona using a VG Quattro (Fisons Instruments, Altrinchman, UK) double quadrupole mass spectrometer in the negative

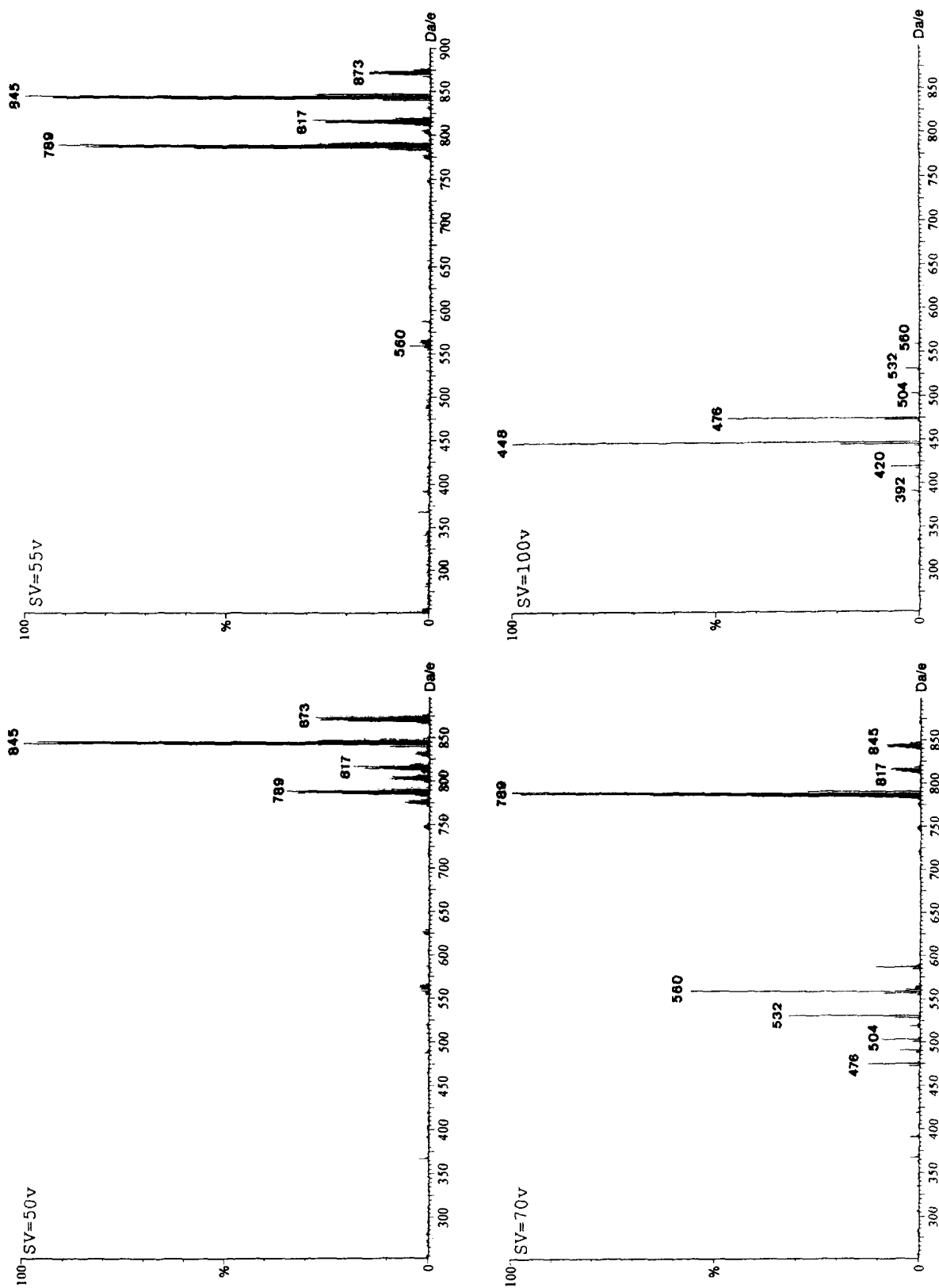


Fig. 2. ESMS spectra of $(\text{PPh}_4)[\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-HgMn}(\text{CO})_3)]$ (5) at different skimmer voltages.

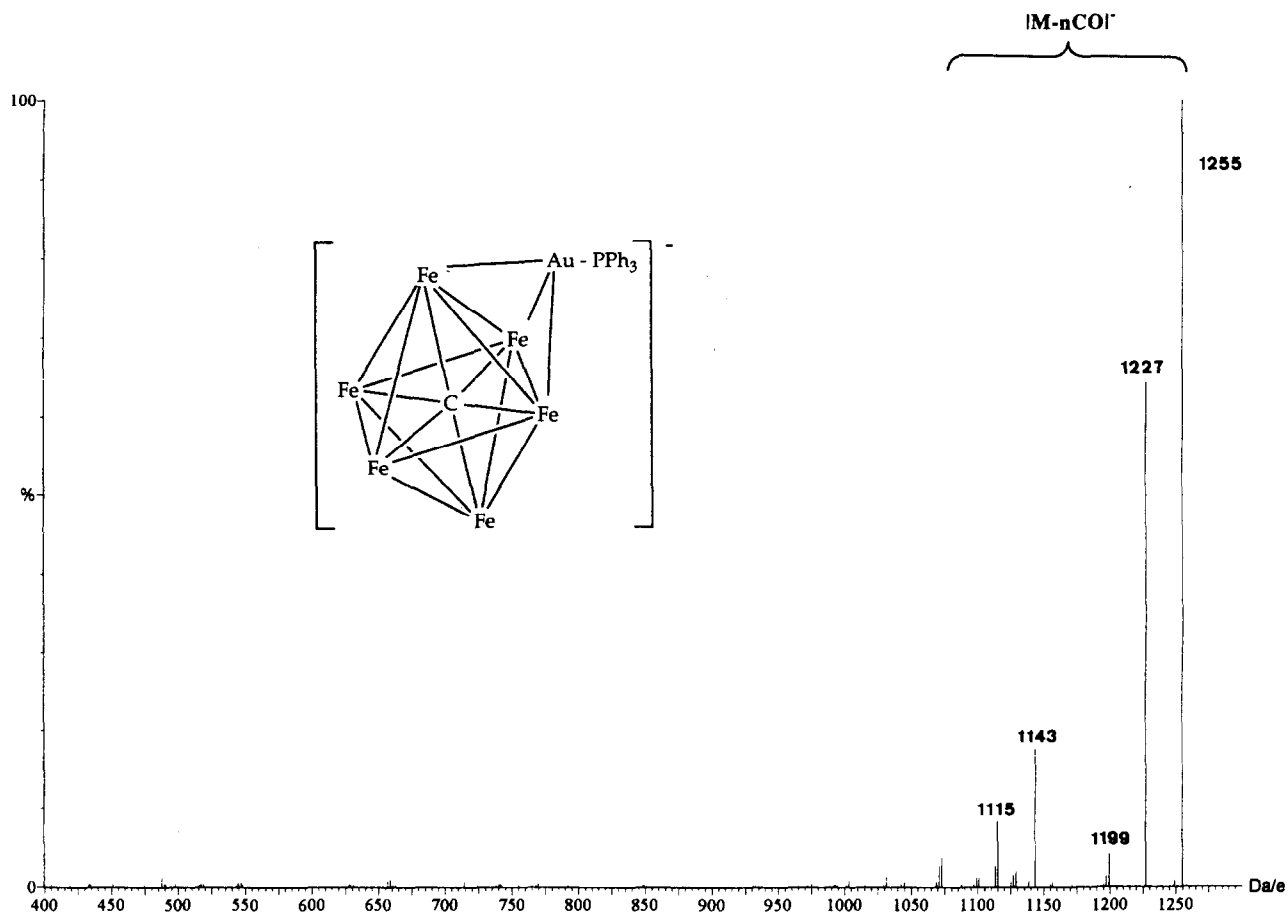
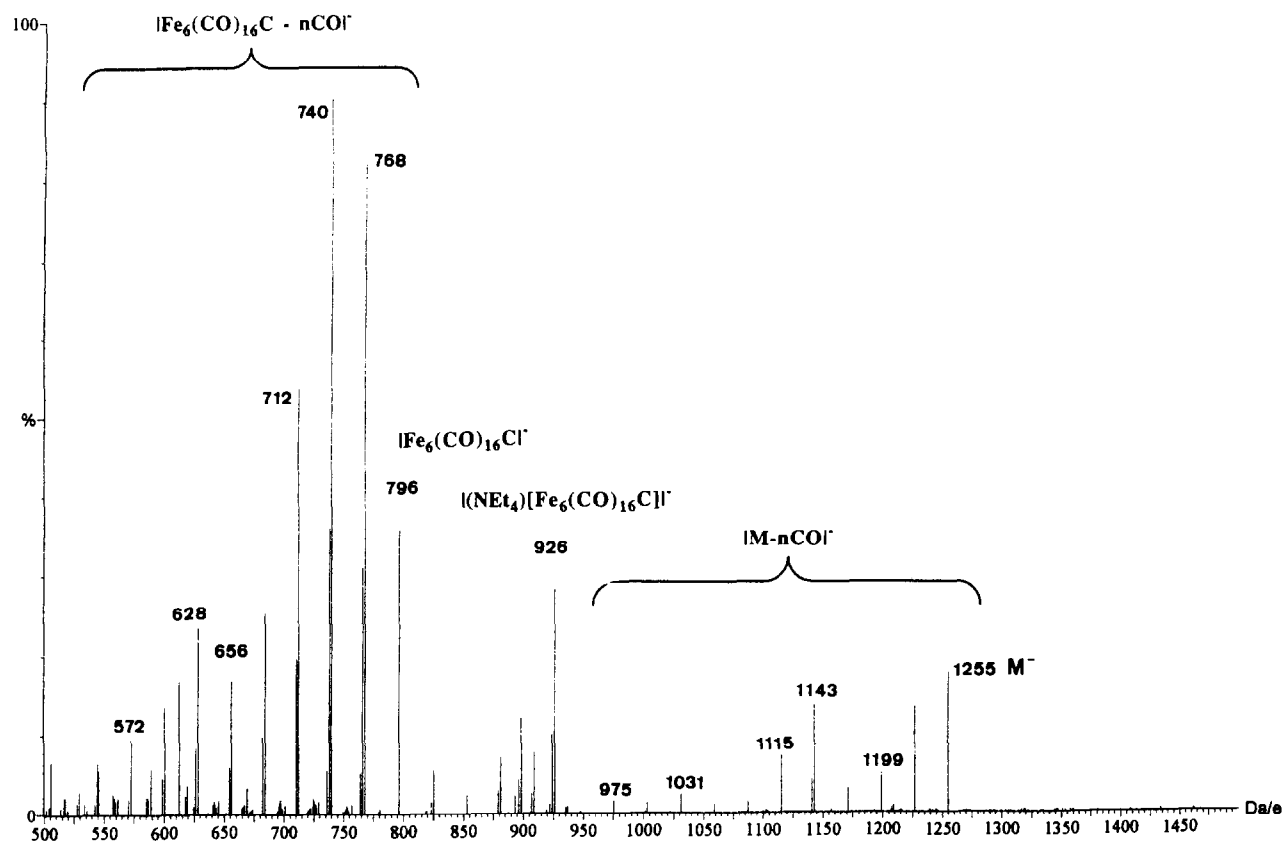


Fig. 3. FAB-MS (top) and ESMS (bottom) spectra of $(\text{NEt}_4)[\text{Fe}_6\text{C}(\text{CO})_{16}\text{AuPPh}_3]$.

ion mode with methanol as mobile phase. All manipulations were performed under an atmosphere of prepurified nitrogen using standard Schlenk techniques. The compounds were dissolved in methanol (2 mM) and this solution was injected directly via a Rheodyne injector with a 10 μl loop to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 7 $\mu\text{L min}^{-1}$. The analyte solution was sprayed from the tip of a needle at about 3.5 kV towards the first skimmer through a counter-current flow of nitrogen. Skimmer voltages of 50, 55, 70 and 100 V were used. Voltages higher than 100 V enhanced the formation of product ions by collision with solvent molecules within the ion source. The scan range was 300–1250 u.

FAB mass spectra were obtained with a VG Quattro quadrupole mass analyser in the negative ion mode. A cesium ion source was used to produce the fast ion beam and the accelerating voltage for the desorbed ions was 10 kV. The mass spectra were acquired by scanning the mass range from 300 to 1500 u using NBA (3-nitrobenzylalcohol) for the matrix.

The molecular masses of the fragment ions are expressed in terms of the largest isotope peak, calculated with the most abundant isotope for each element.

Acknowledgements

We thank Irene Fernández for help in recording the mass spectra. This work was supported by the DGICYT (Project PB93-0766). GS is indebted to the Ministerio de Educación y Ciencia for a scholarship.

References

- [1] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong and C.M. Whitehouse, *Science*, **246** (1989) 64.
- [2] I. Ahmed, A.M. Bond, R. Colton, M. Jurcevic, J.C. Traeger and J.N. Walter, *J. Organomet. Chem.*, **447** (1993) 59; L.A.P. Kane-Maguire, R. Kanitz and M.M. Sheil, *J. Organomet. Chem.*, **486** (1995) 243; V. Katta, S.K. Chowdhury and B.T. Chait, *J. Am. Chem. Soc.*, **112** (1990) 5348; R. Colton, K.L. Harrison, Y.A. Mahand and J.C. Traeger, *Inorg. Chim. Acta*, **231** (1995) 65; Z. Xu, S. Kawi, A.L. Rheingold and B.C. Gates, *Inorg. Chem.*, **33** (1994) 4415; C. Moucheron, C.O. Dietrich-Buchecker, J.P. Sauvage and A. van Dorsselaer, *J. Chem. Soc., Dalton Trans.*, (1994) 885; J.M. Curtis, P.J. Derrick, A. Schnell, E. Constantin, R.T. Gallagher and J.R. Chapman, *Org. Mass. Spectrom.*, **27** (1992) 1176.
- [3] R.L. Cochran, *Appl. Spectrosc. Rev.*, **22** (1986) 137; C. Fenselau and R.J. Cotter, *Chem. Rev.*, **87** (1987) 501.
- [4] S. Naylor and M. Vargas, *J. Organomet. Chem.*, **386** (1990) 275.
- [5] R. Reina, O. Rossell, M. Seco, D. de Montauzon and R. Zquiak, *Organometallics*, **13** (1994) 4300.
- [6] P.J. Krusic, J. San Filippo Jr., B. Hutchinson, R.L. Hance and L.M. Daniels, *J. Am. Chem. Soc.*, **103** (1981) 2129.
- [7] F. Ragaini, D.L. Ramage, J.S. Song and G.L. Geoffroy, *J. Am. Chem. Soc.*, **115** (1993) 12183.
- [8] M.I. Bruce, T.W. Hambley and B.K. Nicholson, *J. Chem. Soc., Dalton Trans.*, (1983) 2385.
- [9] O. Rossell, J. Sales and M. Seco, *J. Organomet. Chem.*, **236** (1982) 415.
- [10] J. Calvet, O. Rossell, M. Seco and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, (1987) 119.
- [11] O. Rossell, M. Seco, G. Segalés and A. Tiripicchio, unpublished results.