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A fast atom bombardment mass spectrometry study of transition metal carbonyl cluster compounds

Stephen Naylor * **and Maria D. Vargas** **
University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW (U.K.)

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Abstract

The use of fast atom bombardment (FAB) mass spectrometry for the characterization of several transition metal cluster compounds is described and compared with that of electron impact (EI) mass spectrometry. The FAB mass spectra of the series $[H_2Os_7(CO)_{22-n}]$ ($n = 0$, 1 and 2) afforded high abundance quasi-molecular ions $[MH]^+$, only when obtained in a CO-saturated 3-nitrobenzyl alcohol (NBA) matrix; loss of CO ligands ($n = 0$, 1) to yield $[H_2Os_7(CO)_{20}]$ occurred in the argon saturated matrix and under the EI mass spectrometry conditions. No molecular signals were detected in the EI mass spectra of the series $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$, $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ and $[(PhMe_2)AuIr_4(CO)_{10}(\mu\text{-}PPh_2)]$, but their FAB mass spectra in NBA matrix displayed $[MH]^+$ ions and fragment ions that are easily correlated to the structures of these species. The FAB mass spectra of compounds $[MIr_4(CO)_9L(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M = Rh, Ir; L = CO, PPh_2Me) in NBA matrix exhibited $[MH]^+$ ions and fragment ions corresponding to loss of CO and of HPh from the PPh ligand. Comparative studies of the reactions of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ and $[(Bu_4N)(Ir_4(CO)_{11}Br)]$ with PPh_3 to give $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ and $[Ir_4(CO)_{11}PPh_3)$, respectively, on the FAB probe tip and in solution have established a correlation between species observed by FAB mass spectrometry and those present in the reaction mixture.

The use of fast atom bombardment mass spectrometry (FAB-MS) [1] to obtain mass spectral data on ionic, non-volatile, thermally labile organometallic compounds has been explored increasingly over the past seven years, and has been reviewed recently [2]. In comparison with electron impact mass spectrometry (EI-MS), where ionization is effected by high energy electrons (~ 70 eV) and

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* Present address: MRC Toxicology Unit, Carshalton, Surrey SM5 4EF, England

** Present address: Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, Campinas 13081, SP, Brazil.

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considerable fragmentation of the molecular ion can occur, FAB-MS results in secondary ions that are only 0–3 eV above their matrix ground state energies [3]. Consequently, FAB-MS of organometallic compounds affords abundant quasi-molecular ions (either $[MH]^+$ or $[M-H]^-$) and significant fragment ions. In FAB-MS, the sample is desorbed directly from a relatively non-volatile, inert liquid matrix, and the choice of a suitable matrix is critical in order to observe an abundant molecular ion.

Until recently, FAB-MS had only been used to aid in structural characterisation of a number of organometallic compounds including transition metal carbonyl clusters ([2] and references therein, [4]), large cationic transition metal gold clusters [5] and polyoxyanions [6]. Transition metal carbonyl clusters with molecular weights > 5000 daltons, e.g. $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$, have been analysed by FAB-MS [7], but with very few exceptions [2,4,8], no attempts to discuss fragmentation patterns or conditions required for obtaining spectra have been made. Also, the presence of a liquid matrix in FAB-MS allows solution chemistry to take place on the FAB-MS probe tip. This phenomenon has been investigated for a variety of compounds including porphyrins [9] and peptide adducts [10], as well as for organometallic compounds [11,12]. In each case a relationship was noted between the processes observed in FAB-MS (e.g., selective loss of ligands) and the known solution chemistry of the compounds under investigation.

In this paper we report our investigations on the use of FAB-MS to study transition metal carbonyl clusters. Firstly, we describe suitable matrix conditions required for obtaining mass spectra as well as conditions to affect the solution chemistry in the matrix in order to detect molecular ions of relatively unstable transition metal carbonyl clusters. Furthermore we demonstrate that FAB-MS may be a powerful tool for the study of the solution chemistry of transition metal carbonyl clusters.

Results and discussion

(1) Sample preparation and choice of matrix

Typically in FAB-MS, the sample is dissolved in a chemically inert, involatile liquid matrix and then bombarded with either high energy atoms or ions. The matrix serves to both dissolve the analyte sample and dissipate the energy of the bombarding fast atoms (ions) before desorbing the analyte into the gas phase [13].

The important role played by the matrix in obtaining a successful FAB-mass spectrum is still often underestimated. The matrix must possess several properties:

(a) the analyte must be soluble in the matrix. For optimum results the analyte must be relatively surface active in order to give a readily discernible molecular ion [14].

(b) the matrix must be chemically inert towards the analyte, e.g., if the analyte is acid sensitive an acidic matrix such as thioglycerol should not be used.

(c) the matrix should be relatively non-volatile in order to allow detection of a molecular ion over a prolonged period of time.

In this study we used a variety of matrices including glycerol (GL) thioglycerol (TG) thiodiglycol (TDG), GL/TG (1/1), tetraglyme, aminoglycerol and 3-nitrobenzylalchol (NBA), in order to obtain FAB mass spectra of transition metal carbonyl clusters.

In general, spectra with the highest relative abundance of both molecular and fragment ions were obtained in NBA, since most of the transition metal carbonyl clusters studied were relatively soluble and gave extended lifetime spectra in this matrix. Good FAB mass spectra of compounds that were insoluble in all matrices noted above, could be obtained by initially dissolving the transition metal carbonyl cluster in an organic solvent such as DMF or CH_2Cl_2 and then adding the solution to the matrix. Although substitution reactions of ligands by the matrix under fast atom bombardment conditions have been observed [15] we have not detected the occurrence of this process with transition metal carbonyl clusters in any of the matrices listed above.

(2) Characterisation of the heptaosmium hydrido clusters $[H_2Os_7(CO)_{22}]$ (1), $[H_2Os_7(CO)_{21}]$ (2) and $[H_2Os_7(CO)_{20}]$ (3)

The EI-MS of the hydrido species **1**–**3** (all fully characterised by X-ray crystallographic analyses [16,17]) were found to be identical and exhibit a "molecular" ion corresponding to $[H_2Os_7(CO)_{20}]^{+}$. This is consistent with the observation that facile conversion of **1** via **2** into **3** by sequential loss of CO occurs in CH_2Cl_2 at room temperature or in cyclohexane under reflux [16] (see Fig. 1).

In contrast the FAB-MS of **1**–**3** afforded abundant molecular ion clusters with $[MH]^+$ at $m/z = 1949$, 1921 and 1893, respectively (using ^{190}Os as the isotope to calculate their molecular weights). Protonated molecular ions ($[MH]^+$) have been observed in FAB-MS for a number of neutral transition metal carbonyl clusters, e.g. $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$ [18], $[(Ph_3PAu)(H)Ru_3(\mu_3\text{-}S)(CO)_9]$ [19] and $[(Ph_3PAu)(H)Fe_4C(CO)_{12}]$ [8], using 18-crown-6/tetraglyme (9/1), glycerol, and carbowax, respectively, as a matrix. However both radical cations $[M]^{+\cdot}$ and $[M+2H]^+$ have also been reported, e.g. the FAB-MS of $[(Ph_3PAu)_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8]$ and $[(Ph_3PAu)_2Ru_3(\mu_3\text{-}S)(CO)_9]$, respectively, both obtained in glycerol [19]. In the present study, as has been observed previously [9,20], the use of NBA, which is a very good electron acceptor, promotes the production of $[M]^{+\cdot}$ ions. Therefore, the abundance of various molecular ion species such as $[M]^{+\cdot}$, $[MH]^+$ or $[M+2H]^+$ and $[M+3H]^+$ are a function of the matrix used. In the present study, for simplicity, we report only the protonated ion $[MH]^+$.

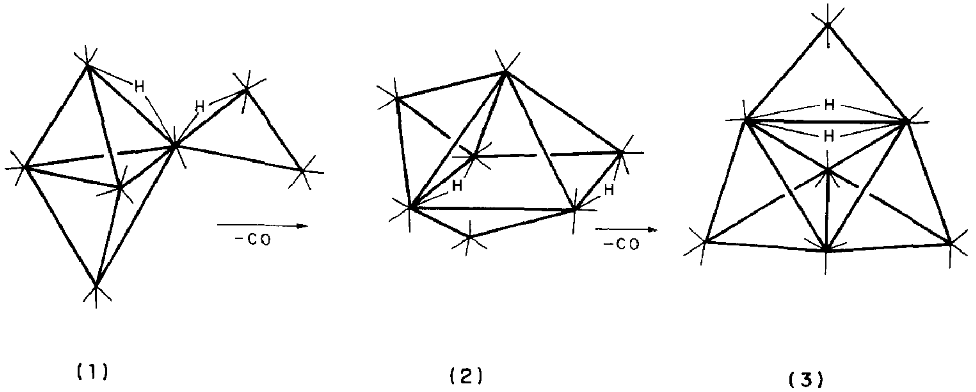


Fig. 1. Structural transformations resulting from the loss of CO ligands in the series $[H_2Os_7(CO)_{22}]$ (1), $[H_2Os_7(CO)_{21}]$ (2) and $[H_2Os_7(CO)_{20}]$ (3).

Table 1

Ions observed in the positive ion FAB-MS of **1**–**3** (with relative ion abundances) using CO saturated NBA as matrix with the samples added in CH_2Cl_2. For the sake of clarity only protonated ions (i.e. $[MH]^+$) are reported using ^{190}Os.

$[H_2Os_7(CO)_{22}]$ (**1**)	m/z = 1949, 12 $[MH]^+$ ($=M'$); 1921, 15 $[M'-CO]^+$; 1893, 13 $[M'-2CO]^+$; 1865, 10 $[M'-3CO]^+$; 1837, 14 $[M'-4CO]^+$; 1809, 8 $[M'-5CO]^+$; 1781, 12 $[M'-6CO]^+$; 1753, 7 $[M'-7CO]^+$; 1725, 15 $[M-8CO]^+$; 1697, 9 $[M'-9CO]^+$; 1669, 8 $[M'-10CO]^+$; 1345, 16 $[M'-Os_2(CO)_8]^+$; 1317, 5 $[M'-Os_2(CO)_8-CO]^+$; 1289, 5 $[M'-Os_2(CO)_8-2CO]^+$.
$[H_2Os_7(CO)_{21}]$ (**2**)	m/z = 1921, 21 $[MH]^+$ ($=M'$); 1893, 20 $[M'-CO]^+$; 1865, 15 $[M'-2CO]^+$; 1837, 17 $[M'-3CO]^+$; 1809, 12 $[M'-4CO]^+$; 1781, 19 $[M'-5CO]^+$ 1753, 11 $[M'-6CO]^+$; 1725, 20 $[M'-7CO]^+$; 1697, 15 $[M'-8CO]^+$; 1669, 9 $[M'-9CO]^+$; 1641, 5 $[M'-10CO]^+$; 1619, 54 $[M'-Os(CO)_4]^+$; 1591, 13 $[M'-Os(CO)_4-CO]^+$; 1563, 14 $[M'-Os(CO)_4-2CO]^+$; 1535, 5 $[M'-Os(CO)_4-3CO]^+$; 1507, 7 $[M'-Os(CO)_4-4CO]^+$; 1479, 4 $[M'-Os(CO)_4-5CO]$.
$[H_2Os_7(CO)_{20}]$ (**3**)	m/z = 1893, 25 $[MH]^+$ ($=M'$); 1865, 12 $[M'-CO]^+$; 1837, 15 $[M'-2CO]^+$, 1809, 9 $[M'-3CO]^+$; 1781, 16 $[M'-4CO]^+$; 1753, 9 $[M'-5CO]^+$; 1725, 13 $[M'-6CO]^+$; 1697, 13 $[M'-7CO]^+$; 1669, 10 $[M'-8CO]^+$.

Table 1 lists the m/z values and relative intensities of the major fragment ions observed for each of the three compounds **1**–**3** in FAB-MS. All spectra were obtained using NBA as the matrix which had been saturated with CO (see Fig. 2 for a representative FAB mass spectrum). When NBA was saturated with argon instead of CO, compounds **2** and **3** exhibited very low abundance quasi-molecular ions ($[MH]^+$) whereas **1** only exhibited an ion at 1893 corresponding to $[\mathbf{1} - 2CO + H]^+$.

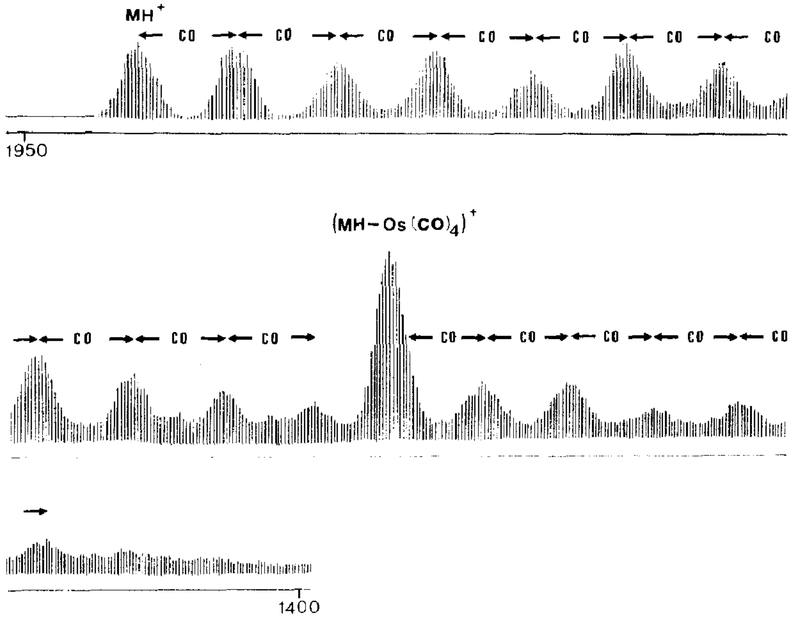


Fig. 2. Positive ion FAB mass spectrum of $[H_2Os_7(CO)_{21}]$ between mass range 1950–1400 daltons, using NBA saturated with CO as matrix.

Loss of CO from **1–3** presumably occurs in the matrix or selvedge region during bombardment. The fact that loss of CO ligands can be avoided in the presence of excess CO in the matrix suggests that ligand dissociation is occurring in the matrix during bombardment and is closely related to the solution chemistry of these compounds [16]. It should be noted that no adduct ions corresponding to $[(M\text{H} + (\text{CO})_n)]^+$ were observed in the presence of CO in the matrix.

The fragmentation patterns in the FAB-MS of **1–3** are similar to those observed in the EI-MS of osmium carbonyl clusters. Both ionization modes afford sequential loss of CO ligands. However, our observations on these and other carbonyl clusters (discussed later) show that in FAB-MS this sequential loss of CO is incomplete. The EI-MS of **3** displays loss of all 20 CO's and the hydride ligands to give an ion corresponding to the mass of the naked $[\text{Os}_7]^{+}$ cation. However, loss of only 8–10 CO ligands is observed in the FAB-MS of **1–3**. The same holds true for homo- and heteronuclear carbonyl clusters also containing other ligands [2,4,8,18,19]. To our knowledge not a single case of total ligand loss to give a naked metal cluster has been detected to date using FAB-MS. This is related to the much softer ionisation conditions associated with FAB-MS compared to EI-MS. The ejection of each CO or other ligand must result in an increase in the electron deficiency within the cluster, leading to a subsequent strengthening of both M–M and M–L bonds occurs. As a consequence the ionization energies accessible during FAB-MS bombardment (0–3 eV above the ground state) are not sufficient to break the M–L bonds after a certain degree of cluster fragmentation.

Transition metal carbonyl clusters **1** and **2**, in addition to sequential CO loss, also exhibit ions corresponding to fragmentation of the metal skeleton in their FAB-MS. This observation can be correlated to their respective solid state structures. The FAB-MS of **2** contains a fragment ion, $m/z = 1619$ corresponding to $[\text{MH} - \text{Os(CO)}_4]^+$. A similar fragment ion, $m/z = 1345$, corresponding to $[\text{MH} - \text{Os}_2(\text{CO})_8]^+$ is also observed in the case of **1**.

The metal geometry of **1** (Fig. 1) consists of a trigonal bipyramidal arrangement of 5 osmium atoms with one of the equatorial atoms linked to an $\text{Os}_2(\text{CO})_8$ unit. Therefore the Os_5 moiety formally acts as a 2 electron donor ligand to $\text{Os}_2(\text{CO})_8$. Similarly in **2** the capped square based pyramidal Os_6 may also be said to formally act as a two electron donor to the edge bridging Os(CO)_4 unit. It may be that the fragments Os(CO)_4 and $\text{Os}_2(\text{CO})_8$ are ejected simply as a result of the gas phase fragmentation process. However, loss of either osmium cluster by chemical reduction in the matrix during bombardment cannot be ruled out.

(3) Characterisation of a series of iridium carbonyl clusters by FAB-MS

The use of FAB-MS to characterise a series of $[\text{Ir}_4(\text{CO})_{12}]$ derivatives has proved to be particularly useful since EI-MS rarely afforded molecular ions for such compounds [21,22]. As part of our studies, we examined the FAB-MS of two series of iridium carbonyl clusters; (i) Ir_4 species containing a phosphido(μ-PPh_2) ligand and (ii) Ir_4M (M = Ir and Rh) clusters containing a phosphinedene (μ_4-PPh) ligand. We were interested in finding correlations between fragmentation patterns in molecules containing similar types of ligands and related molecular structures. Table 2 shows the complexes examined m/z values, and the relative intensities of the principal fragment ions detected.

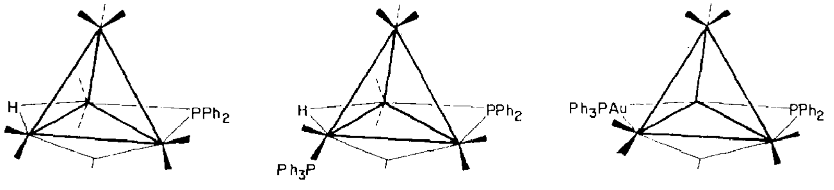
The structures of the phosphido series $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$ (**4**), $[\text{HIr}_4(\text{CO})_9$-

Table 2

Positive ion FAB-MS of a series of iridium carbonyl clusters **4**–**10** using argon saturated NBA as matrix. Only protonated ions are reported for the sake of clarity, using ^{191}Ir.

$[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **(4)**	$m/z = 1231$, 22 $[MH]^+$ $(=M')$, 1203, 5 $[M'-CO]^+$; 1175, 71 $[M'-2CO]^+$; 1147, 68 $[M'-3CO]^+$; 1119, 40 $[M'-4CO]^+$; 1091, 40 $[M'-5CO]^+$; 1063, 37 $[M'-6CO]^+$; 1035, 57 $[M'-7CO]^+$; 1041, 103 $[M'-4CO-HPh]^+$
$[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **(5)**	$m/z = 1465$, 20 $[MH]^+$ $(=M')$; 1437, 23 $[M'-CO]^+$; 1409, 16 $[M'-2CO]^+$; 1381, 63 $[M'-3CO]^+$; 1353, 240 $[M'-4CO]^+$; 1325, 200 $[M'-5CO]^+$; 1297, 180 $[M'-6CO]^+$; 1269, 80 $[M'-7CO]^+$; 1304, 130 $[M'-3CO-HPh]^+$; 1276, 130 $[M'-4CO-HPh]^+$; 1248, 190 $[M'-5CO-HPh]^+$; 1220, 90 $[M'-6CO-HPh]^+$; 1192, 190 $[M'-7CO-HPh]^+$.
$[(Me_2PhP)AuIr_4(CO)_{10}\text{-}(\mu\text{-}PPh_2)]$ **(6)**	$m/z = 1565$, 12 $[MH]^+$ $(=M')$; 1537, 3 $[M'-CO]^+$; 1509, 29 $[M'-2CO]^+$; 1481, 14 $[M'-3CO]^+$; 1453, 19 $[M'-4CO]^+$; 1425, 5 $[M'-5CO]^+$; 1397, 18 $[M'-6CO]^+$; 1369, 14 $[M'-7CO]^+$; 1427, 11 $[M'-PPhMe_2]^+$; 1347, 30 $[M'-5CO-HPh]^+$; 1319, 8 $[M'-6CO-HPh]^+$; 1291, 12 $[M'-7CO-HPh]^+$.
$[Ir_5(CO)_{10}(C_5Me_5)(\mu_4\text{-}PPh)]$ **(7)**	$m/z = 1479$, 24 $[MH]^+$ $(=M')$; 1451, 9 $[M'-CO]^+$; 1423, 41 $[M'-2CO]^+$; 1395, 23 $[M'-3CO]^+$; 1367, 8 $[M'-4CO]^+$; 1339, 17 $[M'-5CO]^+$; 1311, 13 $[M'-6CO]^+$; 1318, 10 $[M'-3CO-Ph]^+$.
$[Ir_4Rh(CO)_{10}(C_5Me_5)\text{-}(\mu_4\text{-}PPh)]$ **(8)**	$m/z = 1391$, 15 $[MH]^+$ $(=M')$; 1363, 6 $[M'-CO]^+$; 1335, 12 $[M'-2CO]^+$; 1307, 9 $[M'-3CO]^+$; 1279, 12 $[M'-4CO]^+$; 1251, 15 $[M'-5CO]^+$; 1223, 10 $[M'-6CO]^+$; 1195, 4 $[M'-7CO]^+$; 1167, 8 $[M'-8CO]^+$; 1230, 13 $[M'-3CO-Ph]^+$.
$[Ir_5(CO)_9(PPh_2Me)(C_5Me_5)\text{-}(\mu_4\text{-}PPh)]$ **(9)**	$m/z = 1651$, 42 $[MH]^+$ $(=M')$; 1623, 8 $[M'-CO]^+$; 1595, 4 $[M'-2CO]^+$; 1567, 29 $[M'-3CO]^+$; 1539, 32 $[M'-4CO]^+$; 1511, 16 $[M'-5CO]^+$; 1483, 12 $[M'-6CO]^+$; 1518, 15 $[M'-2CO-Ph]^+$; 1490, 30 $[M'-3CO-Ph]^+$; 1462, 10 $[M'-4CO-Ph]^+$; 1434, 11 $[M'-5CO-Ph]^+$.
$[RhIr_4(CO)_9(PPh_2Me_5)\text{-}(\mu_4\text{-}PPh)]$ **(10)**	$m/z = 1563$, 200 $[MH]^+$ $(=M')$; 1535, 40 $[M'-CO]^+$; 1507, 30 $[M'-2CO]^+$, 1479, 65 $[M'-3CO]^+$; 1451, 74 $[M'-4CO]^+$; 1423, 71 $[M'-5CO]^+$; 1430, 120 $[M'-2CO-Ph]^+$; 1402, 40 $[M'-3CO-Ph]^+$; 1374, 63 $[M'-4CO-Ph]^+$; 1346, 21 $[M'-5CO-Ph]^+$.

$(PPh_3)(\mu\text{-}PPh_2)]$ **(5)** and $[(PhMe_2)Au\ Ir_4(CO)_{10}(\mu\text{-}PPh_2)]$ **(6)** have all been established by X-ray diffraction studies [23,24] and are shown in Fig. 3. For each compound no molecular ion signals were detected in EI-MS. Molecular ions corresponding to $[MH]^+$ were detected in the positive ion FAB-MS of **4**–**6** and the fragment ions observed were easily correlated to the structures of the three iridium clusters. A sequential loss of seven CO ligands for **4**–**6** was observed as well as loss of a phenyl group. A comparison of the intensities of the peaks resulting from the loss of the phenyl group (**4**: $m/z = 1041$ $[MH-4CO-HPh]^+$; **5**: $m/z = 1304$ $[MH-3CO-HPh]^+$ and **6**: $m/z = 1347$ $[MH-5CO-HPh]^+$) suggests that these three abundant ions relative to the rest of the spectra are the result of loss of HPh from the PPh_2 ligand rather than from the PPh_3 in **5** or the Me_2PhP in **6**. These results are in agreement with recent findings of the solution chemistry of the

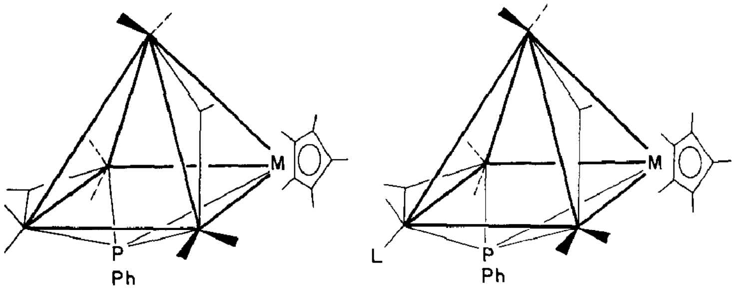


(4) (5) (6)

Fig. 3. Schematic structures of the cluster compounds $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ (4), $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ (5) and $[(Me_2PhP)AuIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ (6).

cluster $[HRu_3(CO)_{10}(\mu\text{-}PPh_2)]$. Under reflux in toluene this compound yields $[Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2]$, presumably via HPh loss and cluster fragmentation and recombination [25]. It should be noted that loss of PPh_3 from **5** is not observed, while an intense peak resulting from the loss of $PPhMe_2$ (m/z 1428, $[M\text{H} - PPhMe_2]^+$) can be seen in the FAB mass spectrum of **6**. These FAB-MS results concur with the solution chemistry of **5** and **6**. The $PPhMe_2$ ligand of **6** is readily substituted in CH_2Cl_2 by $L = P(4\text{-}OMeC_6H_4)_3$, a stronger nucleophile, to yield $[LAuIr_4(CO)_{10}(\mu\text{-}PPh_2)]$. The PPh_3 ligand in **6** is not substituted under the same reaction conditions [24]. Dissociation of both the $AuPR_3$ fragment and the PR_3 ligand from mixed metal carbonyl cluster in FAB-MS is a common phenomenon [19] and in several cases can be correlated to the solution chemistry of these cluster compounds. For example, addition of X_2 (X = Cl, Br, I) to $[Os_{10}C(CO)_{24}(AuPPh_3)]^-$ results in the formation of $[Os_{10}C(CO)_{24}(\mu\text{-}X)]^-$ [26], while oxidation of the same species results in cluster condensation to give $[Os_{20}Au(C)_2(CO)_{48}]^{2-}$, via loss of PPh_3 [7]. In addition, facile dissociation of the $AuPR_3^+$ moiety is often observed in the presence of donor ligands (e.g. phosphines and halides) or in polar solvents such as THF, acetone or CH_3CN [26], therefore the correct choice of the cosolvent and matrix for the FAB experiment is crucial in these cases.

The structures of the phosphinedene series $[MIr_4(CO)_{10}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M = Ir (**7**), Rh (**8**) and $[MIr_4(CO)_9(PPh_2Me)(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M = Ir (**9**), Rh (**10**)) are shown in Fig. 4. The initial characterisation was based on FAB-MS and microanalysis. On the basis of Wade rules [27] a structure consisting of a square-



(a) (b)

Fig. 4. Schematic structures of the pentanuclear cluster compounds (a) $[MIr_4(CO)_{10}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M = Ir (**7**), Rh (**8**)); (b) $[MIr_4(CO)_9(PPh_2Me)(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$, (M = Ir (**9**), Rh (**10**)).

Table 3

EI-MS of compounds **7**–**10** using ^{191}Ir to report molecular ions

Compound	EI-MS
7	1478 $[M]^{+}$
	1478 − 28x, $x = 1$–10 $[M-(\mathrm{CO})_x]^{+}$
8	1390 $[M]^{+}$
	1390 − 28x, $x = 1$–10 $[M-(\mathrm{CO})_x]^{+}$
9	1542 $[M-108]^{+}$
	1542 − 28x, $x = 1$–9 $[M-\mathrm{Ph}-(\mathrm{CO})_x]^{+}$
10	1454 $[M-108]^{+}$
	1454 − 28x, $x = 1$–9 $[M-\mathrm{Ph}-(\mathrm{CO})_x]^{+}$

based arrangement of metal atoms with the phosphinedene ligand capping the square face had been proposed for these 74 electron species. This arrangement has recently been confirmed by X-ray analyses of the compound **7** and $[\mathrm{MIr_4(CO)_9(PPh_3)(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)}]$ [28].

In the FAB-MS of **7**–**10** using NBA as the matrix, sequential loss of CO ligands was noted in preference to loss of $[\mathrm{C_5Me_5}]$ or $[\mathrm{PPh_2Me}]$. The spectra of **7**–**10** also exhibited fragment ions corresponding to the loss of HPh. These peaks, which are relatively abundant in the case of the $\mathrm{PPh_2Me}$ substituted clusters **9** and **10** ($m/z = 1518$ and 1430, respectively) correspond to the ions $[M\mathrm{H}-2\mathrm{CO}-\mathrm{Ph}]^{+}$ and presumably reflect the loss of Ph from PPh rather than from the $\mathrm{PPh_2Me}$ ligand, since a similar process is observed in the FAB-MS of **7** and **8** ($m/z = 1318$ and 1230, respectively), which give rise to $[M\mathrm{H}-3\mathrm{CO}-\mathrm{Ph}]^{+}$ ions. It has been pointed out before [2] that the mass spectra of organometallic compounds using FAB or EI gives rise to different fragment ions. It is interesting that the EI-MS of **7** and **8** both exhibit, in addition to their parent molecular ions $[M]^{\dot{+}}$, ions resulting from sequential loss of 10CO ligands, and ions corresponding to the fragment $[M-4\mathrm{CO}-\mathrm{Ph}]^{+}$ (Table 3). In contrast, the EI-MS of the $\mathrm{PPh_2Me}$ substituted compounds **9** and **10** do not show parent molecular ions ($[M]^{\dot{+}}$) (Table 3); the highest mass ion for both species corresponds to the $[M-\mathrm{CO}-\mathrm{Ph}]^{\dot{+}}$ ion, followed by ions arising from sequential loss of 8CO ligands. Clean loss of the $\mathrm{PPh_2Me}$ or $\mathrm{C_5Me_5}$ ligands is not observed in either spectrum.

(4) Use of FAB-MS to study the solution chemistry of some Ir_4 clusters

The study of the reactions of transition metal carbonyl clusters is not a simple task. The reactions are rarely specific, often giving a number of side-reaction products in low yields which can seldom be characterised. In addition, reaction intermediates are only isolated and characterised in rare cases, making it difficult to understand the mechanism by which such reactions proceed. Following the successful use of FAB-MS to elucidate the mechanism of complex organometallic reactions (see ref. 2 for examples) we applied this technique to study the reactions of the tetrairidium carbonyl cluster compound, $[\mathrm{HIr_4(CO)_{10}(\mu\text{-}PPh_2)}]$ (**4**) with $\mathrm{PPh_3}$. Reaction of $[\mathrm{HIr_4(CO)_{10}(\mu\text{-}PPh_2)}]$ (**4**) with $\mathrm{PPh_3}$ (1/1 or 1/10 in $\mathrm{CH_2Cl_2}$) gives, as the only product detected by IR spectroscopy, $[\mathrm{HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)}]$ (**5**) [23]. Kinetic studies of the reaction of **4** with a variety of phosphines under pseudo-first order conditions, have established that these reactions occur via an associative mechanism [29]. The first step of the reaction is the formation of the 62 electron adduct $[HIr_4(CO)_{10}(PPh_3)(\mu\text{-}PPh_2)]$ as either a transition state or intermediate by nucleophilic attack at an iridium centre. We used FAB-MS as a means of detecting the proposed adduct as well as to look for the presence of any other side reaction products and to follow the reaction to completion. Aliquots of the reaction mixture containing **4** and PPh_3 (1/10) were added to NBA after various time points, and the FAB-MS was obtained. The only compounds detected were the starting material **4** and the final product **5** whose FAB-MS were described in Table 2. Progressive decrease in the abundance of the molecular ion $[MH]^+$ of (**4**) was noted until it could no longer be detected after 4 h. Similarly **4** and **5** were the only compounds detected when the freshly made reaction mixture was added to NBA and allowed to stand on the FAB probe tip for 10 min. The reaction mixture was monitored every two minutes using FAB-MS and showed a concomitant decrease in the abundance of the **4** $[M+H]^+$ ions and increase in that of **5** $[M+H]^+$ ions. It is clear that under bombardment conditions, species other than those formed in solution are not generated * e.g. products from further CO substitution by excess PPh_3 in the mixture. Thus, in this system a correlation between species observed by FAB-MS spectroscopy and those present in the reaction mixture has been established. Failure to detect the $[HIr_4(CO)_{10}(PPh_3)(\mu\text{-}PPh_2)]$ species suggests that it is either a transition state or a highly unstable, short-lived intermediate, and the mechanism of this CO substitution reaction is best described in terms of an interchange pathway of the type Ia [30].

(5) Characterization of $[(Bu_4N)(Ir_4(CO)_{11}Br)]$ (11) and study of its reactivity with PPh_3

The FAB-MS of $[(Bu_4N)(Ir_4(CO)_{11}Br)]$ (**11**) was obtained in both positive and negative ion mode and the results are outlined in Table 4. The positive ion FAB-MS of (**11**) afforded an ion of low signal ion abundance at $m/z = 1402$ corresponding to $[(Bu_4N)(Ir_4(CO)_{11}Br) + H]^+$ as well as an intense fragment ion at $m/z = 1080$ due to loss of Br from $[Ir_4(CO)_{11}Br]^-$. Loss of a halide ligand has been noted as a major fragmentation pathway in organometallic compounds, e.g. $[M(CO)Cl(PPh_3)_2]$ (M = Rh, Ir) [31] and RuCl(bipy)Cp [32]. In several cases this loss has been related to the

Table 4

Positive and negative ion FAB-MS of the reaction between $[(Bu_4N)(Ir_4(CO)_{11}Br)]$ (**11**) + PPh_3

Compound	Positive ion FAB-MS		Negative ion FAB-MS	
	m/z Assignment	Ion Intensity	m/z Assignment	Ion Intensity
$[(Bu_4N)(Ir_4(CO)_{11}Br)]$	1402 $[MH]^+$	8	1159 $[Ir_4(CO)_{11}Br$	40
	1080 $[Ir_4(CO)_{11}H]^+$	35	see consecutive loss of 8 CO's	
11 + PPh_3	1343 $[Ir_4(CO)_{11}PPh_3]^+$	38	1342 $[(Ir_4(CO)_{11}PPh_3)-H]^-$	4
			1314 loss of CO	48

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* CO substitution in **4** by PhC≡CPh does not occur in solution under the conditions observed for the reaction with PPh_3. No reaction was observed either when this mixture was allowed to stand on the FAB probe under the same conditions as the mixture of **4** plus PPh_3.

solution chemistry of the compound e.g. [*mer*-$OsCl_3(PMe_2Ph)_3$] (highest mass ion observed $[M-Cl]^+$) for which the dominant reaction is loss of Cl^- rather than PMe_2Ph [33]. In negative ion FAB-MS an abundant ion at $m/z = 1159$ corresponding to $[Ir_4(CO)_{11}Br]^-$ was detected as well as ions due to sequential loss of 8 CO ligands. No peak corresponding to $[Ir_4(CO)_{12}]$ at $m/z = 1108$, was observed in either the positive or negative ion spectra (even when the NBA matrix was saturated with CO). However addition of 5 equivalents of PPh_3 in THF to **11** to the NBA matrix yielded an ion at $m/z = 1343$ and 1341 corresponding to $[Ir_4(CO)_{11}PPh_3]$ (**12**), in positive and negative ion FAB-MS, respectively.

The formation of $[Ir_4(CO)_{11}PPh_3]$ (**12**) on the probe mimics the solution chemistry of **11**. Indeed, compounds such as $[Ir_4(CO)_{11}L]$ ($L = PR_3$, $P(OR)_3$) are synthesized by displacement of the bromide ligand in **11** by the desired tertiary phosphine or phosphite in CH_2Cl_2 [34]. It is interesting to note that **12** does not undergo CO substitution with excess PPh_3 to yield $[Ir_4(CO)_{10}(PPh_3)_2]$ (**13**) under FAB conditions. In comparison, reaction of **12** with PPh_3 in chlorobenzene at 80–90 °C gives **13** and $[Ir_4(CO)_9(PPh_3)_3]$ [35], which suggests that the reaction conditions in the FAB matrix are milder than those described above.

Experimental

Materials: Glycerol, thioglycerol, aminoglycerol thiodiglycol and 3-nitrobenzylalcohol were all purchased from Sigma Chemical Co. (UK.), and distilled under vacuum prior to use. Triphenyl phosphine was purchased from Aldrich Chemical Co. (UK), and used without further purification.

Synthesis: The compounds $[H_2Os_7(CO)_{22}]$, $[H_2Os_7(CO)_{21}]$ [16]; $[H_2Os_7(CO)_{20}]$ [17]; $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$, $[(Ph_3P)AuIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ [36]; $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ [23]; $[MIr_4(CO)_9L(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (where $M = Ir$, Rh; $L = CO$, PPh_2Me) [28]; $[(Bu_4N)(Ir_4(CO)_{11}Br)]$ [37]; and $[Ir_4(CO)_{11}PPh]$ [36] were prepared and purified according to previously published procedures. Unless otherwise stated all experiments were carried out under dry, oxygen free, nitrogen with solvents dried and distilled (under N_2) prior to use.

Mass Spectra: Sample preparation. The transition metal carbonyl cluster in solution (usually CH_2Cl_2) was added to ~ 2 μl of matrix on an acid-etched stainless steel probe tip and thoroughly mixed, then subjected to FAB mass spectrometry. Matrices were treated by bubbling either Ar or CO through them for two hours prior to their use in FAB-MS.

All EI-MS were recorded on a Kratos MS-12 as described previously [26]. All FAB-MS were recorded on a Kratos MS50 instrument operating at 8 KeV. The instrument was equipped with a standard Kratos FAB source and an Ion Tech Gun. The energy of the primary atom beam was 8 KeV at an ion current of 400 μA. Xenon was used as the source of high energy atoms. Spectra were obtained with a magnet scan rate in the range 30–100 seconds per decade using a magnet of 10.000 daltons mass range at 8 KeV. The source pressure was typically $\sim 1.3 \times 10^{-3}$ Pa.

Conclusion

This work has confirmed the importance of FAB-MS in the study of high nuclearity transition metal carbonyl clusters. In the case of transition metal carbonyl clusters which do not contain active nuclei for NMR studies, apart from X-ray crystallography, FAB-MS is the most useful technique for structural analysis of such compounds. For example, reactions can be monitored and information on solution species can be obtained using exceedingly small quantities of compounds (eg ~ 1 nmol). In one case we show that under bombardment conditions, substitution reactions of specific transition metal carbonyl cluster ligands can be observed. This is particularly valuable for determining the reactivity of high nuclearity transition metal carbonyl clusters which are almost always available in limited amounts.

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