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Electrospray mass spectrometric studies of some cationic and anionic Group 6 and Group 7 metal carbonyl complexes

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Abstract

Electrospray mass spectra derived from dichloromethane or dichloromethane/methanol solutions of cationic and anionic metal carbonyl compounds are reported for the first time. The cations investigated are the seven coordinate species $[M(CO)_2(P\text{–}P)_2X]^+$ (M = Mo, W; P–P = diphosphine or similar ligand; X = F, Cl, Br, I) and carbonyl phosphonium or arsonium cations of the types $[M(CO)_3(\eta^1\text{-P–PMe})(\eta^2\text{-P–P})]^+$ (M = Cr, Mo, W), $[M'(CO)_2(\eta^1\text{-P–PMe})(\eta^2\text{-P–P})X]^+$ (M′ = Mn, Re). These cations were prepared by the action of MeI on $M(CO)_3(\eta^1\text{-P–P})(\eta^2\text{-P–P})$ and $M'(CO)_2(\eta^1\text{-P–P})(\eta^2\text{-P–P})X$, respectively, each of which contains a pendant Group 15 atom. The anionic species investigated are $[M(CO)_5X]^-$ and $[M'(CO)_4X_2]^-$. In all cases the dominant peak in the mass spectrum corresponds to the principal ion known to be present in solution.

1. Introduction

Mass spectrometry of inorganic and organometallic compounds has often involved volatilizing the species prior to forming ions in the gas phase and most early studies where therefore performed on neutral compounds. The original ionization technique involving electron impact (EI) frequently led to extensive fragmentation, especially for metal carbonyl compounds, although the molecular ion was sometimes observed as a low intensity peak [1]. Consequently, many efforts have been made to devise softer ionization techniques and fast atom bombardment mass spectrometry (FAB/MS) has been one of the more successful. In the study of neutral species, it often generates the molecular ion [2] and in the case of ionic compounds there have been numerous cases in which the principal ion has been observed [3–5]. The term "principal ion" is used [6] in situations in which the original species and that observed in the gas phase are the same. The term "molecular ion" is reserved for situations where a neutral species is converted into an ion of the same molar mass in the gas phase.

Electrospray mass spectrometry (ESMS) provides a new method of transferring pre-existing ions from solution to the gas phase. The transfer is very soft and causes minimal fragmentation. ESMS is a now well established technique in the structural analysis of large biomolecules such as proteins [7,8]. These are protonated with an organic acid and a family of peaks is observed corresponding to different degrees of protonation of the protein. For example, horse heart myoglobin (mol. wt. 16951) gives peaks in the *m/z* region 700–1700, corresponding to intact molecules with the addition of 10–24 protons, which can be used to calculate the molecular weight of the protein. However, although the biochemical applications demonstrate that ESMS links solution and gas phase studies, the technique has not been applied systematically to inorganic and organometallic systems.

We have recently been investigating the use of ESMS on a wide range of charged inorganic and organometallic compounds. Anions and cations for which ES mass spectra have been obtained from solution include $[Fe(C_5H_5)_2]^+$, $[PF_6]^-$ and $[S_2Mo_{18}O_{62}]^{4-}$ [9]. We have also undertaken detailed studies of the ES mass spectra of a series of platinum cations of the type $[(P\text{–}P)Pt(S\text{–}S)]^+$ (P–P = diphosphine or similar ligand; S–S = dithiolate ligand) [10] and of phosphonium cations derived from a number of polyphosphines [11]. A fea-

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ture of these studies was that the principal ions were always observed, often as the only significant peak in the mass spectrum, emphasizing the soft nature of the process generating gas phase ions. In this paper we report for the first time a detailed application of ESMS to solutions of both cationic and anionic metal carbonyl derivatives.

The oxidation of $Mo(CO)_2(dpe)_2$ [12] (dpe = $Ph_2PCH_2CH_2PPh_2$) by various means has been investigated by several workers [13–16], with conflicting interpretations of the results. However, in a significant study Snow and Wimmer [17] showed that in dichloromethane the products of the reaction between $Mo(CO)_2(dpe)_2$ and $NOPF_6$ are first *trans*-$[Mo(CO)_2(dpe)_2]^+$ and subsequently $[Mo(CO)_2(dpe)_2F]^+$ (the fluoride being extracted from PF_6^-). They also prepared the complete series $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br, I) by oxidation of $Mo(CO)_2(dpe)_2$ with $NOPF_6$ in the presence of the appropriate halide. The oxidation of the corresponding derivatives of dpm (dpm = $Ph_2PCH_2PPh_2$) have not been investigated so widely, and on the basis of the available data there appears to be some significant differences between the two systems. We have previously shown [18] that oxidation of $M(CO)_2(dpm)_2$ (M = Cr, Mo, W) with $O_2/HClO_4$ yields the divalent hydride cation $[M(CO)_2(dpm)_2H]^+$ rather than $[M(CO)_2(dpm)_2]^+$, although the monovalent cations can be observed on the voltammetric timescale by electrochemical oxidation of $M(CO)_2(dpm)_2$. We have re-prepared these compounds and observed their ES mass spectra, and characterized some of the corresponding dpm halocarbonyl complexes and their tungsten analogues for the first time by their ES mass spectra.

Compounds of the types $M(CO)_3(\eta^1\text{-P-P})(\eta^2\text{-P-P})$ [19,20] and $M'(CO)_2(\eta^1\text{-P-P})(\eta^2\text{-P-P})X$ [21–23] (M = Cr, Mo, W; M′ = Mn, Re; X = Cl, Br, I) are well known. These compounds are neutral and therefore not observable by ESMS, but reaction with MeI converts the pendant Group 15 atoms into the corresponding phosphonium or arsonium cations to give $[M(CO)_3(\eta^1\text{-P-PMe})(\eta^2\text{-P-P})]^+$ and $[M'(CO)_2(\eta^1\text{-P-PMe})(\eta^2\text{-P-P})X]^+$, in which the oxidation states of the metals are unchanged, and these have been observed by ESMS.

We have also investigated by ESMS the known anionic species $[M(CO)_5X]^-$ [24] and $[M'(CO)_4X_2]^-$ [25] in order to illustrate the use of the technique for carbonyl anions.

2. Results

Throughout this paper, peaks in the mass spectra are identified by the m/z value of the strongest peak in the isotopic mass distribution. In all cases the experimental isotopic mass distributions agreed with the calculated pattern.

2.1. Seven coordinate cations of Mo and W

When $Mo(CO)_2(dpe)_2$ (2 mM) in dichloromethane is oxidized by $NOBF_4$ and the ES mass spectrum of a diluted (0.2 mM) sample of the solution is acquired at a low ion source voltage (B1 voltage ~30 V, see Experimental section) within a few minutes, it is dominated by the peak due to $[Mo(CO)_2(dpe)_2]^+$ (m/z 950) with only a small peak due to $[Mo(CO)_2(dpe)_2F]^+$ (m/z 969). If after about 15 min a new dilution and data acquisition are performed, the peak due to the seven coordinate Mo^{II} fluoro-cation is found to have become dominant, thus confirming the observations by Snow and Wimmer [17]. The fluoro-cation is formed more quickly if the oxidation is performed in the presence of the soluble fluoride $[Ph_3PBz][H_2F_3]$ [26]. The overall reaction is consistent with a disproportionation reaction, as shown in eq. (1),

$$2[Mo(CO)_2(dpe)_2]^+ \rightarrow Mo(CO)_2(dpe)_2 + [Mo(CO)_2(dpe)_2]^{2+} \quad (1)$$

followed by addition of fluoride to the 16-electron dication, although mechanistic details are unknown. Similar overall disproportionations have been observed for a number of other 17-electron carbonyl compounds [27–29]. When the ion source voltage (B1) is increased to 60–70 V, loss of one or both carbonyl ligands from the principal ion is observed. This is caused by collisions of the principal ions with solvent molecules in the vicinity of the evaporation nozzle where the pressure is close to atmospheric. Data for all the halocarbonyl principal cations described in this paper are given in Table 1.

When the NO^+ oxidation of $Mo(CO)_2(dpe)_2$ is carried out in the presence of a different halide, the 17-electron $[Mo(CO)_2(dpe)_2]^+$ cation is again observed initially, but after some minutes of reaction the ES mass spectrum usually shows peaks due to $[Mo(CO)_2(dpe)_2X]^+$ and $[Mo(CO)_2(dpe)_2H]^+$. Similarly, oxidations of $Mo(CO)_2(dpe)_2$ with bromine or iodine in dichloromethane give ES mass spectra that at first show only the principal ion $[Mo(CO)_2(dpe)_2]^+$, but again after a few minutes new dilutions of the bulk solution give mass spectra showing peaks due to both $[Mo(CO)_2(dpe)_2X]^+$ and $[Mo(CO)_2(dpe)_2H]^+$ as the reaction proceeds. It is significant that the hydride cation is seen only after the appearance of the halocarbonyl cation, which suggests that the hydride is formed from the halocarbonyl cation within the mass spectrometer by reaction with the mobile phase, which contains $MeOH/H_2O$ and acetic acid. This was confirmed by isolating samples of several of the halocarbonyl cations and examination of their ^1H and ^{31}P NMR spectra. In all cases the data agreed with literature values [17] and showed no evidence of the presence of the hydride cation, even in the presence of dilute acetic acid. However, the ES mass spectra showed peaks due to the hydride $[Mo(CO)_2(dpe)_2H]^+$ as well as the halocarbonyl cations $[Mo(CO)_2(dpe)_2X]^+$.

The ES mass spectrum resulting from the interaction of $Mo(CO)_2(dpm)_2$ with $NOBF_4$ in dichloromethane or acetone showed $[Mo(CO)_2(dpm)_2H]^+$ as the principal ion, and the ion $[Mo(CO)_2(dpm)_2]^+$ was never observed. It appears therefore, that $[Mo(CO)_2(dpm)_2]^+$ is protonated much more rapidly than the corresponding dpe compound, so that the fluoro derivative is not formed. When $Mo(CO)_2(dpm)_2$ was oxidized with bromine or iodine in dichloromethane at room temperature, the ES mass spectrum gave only a peak for the principal ion $[Mo(CO)_2(dpm)_2X]^+$ with no evidence for the formation of the hydride cation. The dpm halo cations are less labile than their dpe analogues, and do not react with the solvent within the ion source. Oxidation of $W(CO)_2(dpm)_2$ gave very similar results (Table 1), and this is the first time some of these derivatives have been reported.

TABLE 1. Electrospray mass spectra of carbonyl cations of Mo^{II} and W^{II}

Compound	Oxidant	Solvent	Principal ions (*m/z*) [a]
$Mo(CO)_2(dpm)_2$	$NOBF_4$	CH_2Cl_2	$[Mo(CO)_2(dpm)_2H]^+$ (922)
	Br_2	CH_2Cl_2	$[Mo(CO)_2(dpm)_2Br]^+$ (1001)
	I_2	CH_2Cl_2	$[Mo(CO)_2(dpm)_2I]^+$ (1049)
$Mo(CO)_2(dpe)_2$	$NOBF_4$	CH_2Cl_2	$[Mo(CO)_2(dpe)_2]^+$ (950)
	$O_2/HClO_4$	Acetone	$[Mo(CO)_2(dpe)_2H]^+$ (951)
	$NOBF_4 + F^-$	CH_2Cl_2	$[Mo(CO)_2(dpe)_2F]^+$ (969)
	$NOBF_4$	Acetone	$[Mo(CO)_2(dpe)_2F]^+$ (969)
	$NOBF_4 + Cl^-$	Acetone	$[Mo(CO)_2(dpe)_2Cl]^+$ (985)
	Br_2	CH_2Cl_2	$[Mo(CO)_2(dpe)_2Br]^+$ (1029)
	I_2	CH_2Cl_2	$[Mo(CO)_2(dpe)_2I]^+$ (1077)
$W(CO)_2(dpm)_2$	$NOBF_4$	CH_2Cl_2	$[W(CO)_2(dpm)_2H]^+$ (1009)
	Br_2	CH_2Cl_2	$[W(CO)_2(dpm)_2Br]^+$ (1089)
	I_2	CH_2Cl_2	$[W(CO)_2(dpm)_2I]^+$ (1135)
$W(CO)_2(dpe)_2$	$NOBF_4$	CH_2Cl_2	$[W(CO)_2(dpe)_2]^+$ (1036)
	$O_2/HClO_4$	Acetone	$[W(CO)_2(dpe)_2H]^+$ (1037)
	$NOBF_4 + F^-$	CH_2Cl_2	$[W(CO)_2(dpe)_2F]^+$ (1055)
	Br_2	CH_2Cl_2	$[W(CO)_2(dpe)_2Br]^+$ (1115)
	I_2	CH_2Cl_2	$[W(CO)_2(dpe)_2I]^+$ (1163)

[a] Strongest peak in the isotopic mass distribution.

2.2. *Compounds of the types* $[M(CO)_3(\eta^1\text{-}P\text{-}PMe)(\eta^2\text{-}P\text{-}P)]^+$ *and* $[M'(CO)_2(\eta^1\text{-}P\text{-}PMe)(\eta^2\text{-}P\text{-}P)X]^+$

The ^{31}P NMR spectra of the complexes *fac*- or *mer*-$M(CO)_3(\eta^1\text{-}P\text{-}P)(\eta^2\text{-}P\text{-}P)$ and $M'(CO)_2(\eta^1\text{-}P\text{-}P)(\eta^2\text{-}P\text{-}P)X$ in deuterochloroform solution each show resonances due to three coordinated phosphorus atoms and one close to the resonance position of the free ligand, which is assigned to the pendant phosphine [19–23]. In all cases, upon reaction with MeI at room temperature the pendant phosphorus resonance disappears and is replaced by a new resonance at higher frequency in the region associated with phosphonium salts. The positions of the other resonances are essentially unchanged, indicating that the rest of the molecule is unaffected by the reaction with MeI and the products are $[M(CO)_3(\eta^1\text{-}P\text{-}PMe)(\eta^2\text{-}P\text{-}P)]^+$ and $[M'(CO)_2(\eta^1\text{-}P\text{-}PMe)(\eta^2\text{-}P\text{-}P)X]^+$. Similar reactions have been reported previously for some of the manganese and rhenium compounds [21,23].

The ES mass spectrum of $[Cr(CO)_3(\eta^1\text{-}dpmMe)(\eta^2\text{-}dpm)]^+$ is dominated by a peak at *m/z* 919 which is due to the principal ion. Another peak at *m/z* 399 is assigned to $dpmMe^+$, which is formed by collisional activation in the ion source. All the other Group 6 $[M(CO)_3(\eta^1\text{-}P\text{-}PMe)(\eta^2\text{-}P\text{-}P)]^+$ cations gave analogous mass spectra and the data are given in Table 2.

The ES mass spectrum of $[Re(CO)_2(\eta^1\text{-}dpmMe)(\eta^2\text{-}dpm)Cl]I$ shows a strong peak at *m/z* 1061, due to the principal ion $[Re(CO)_2(\eta^1\text{-}dpmMe)(\eta^2\text{-}dpm)Cl]^+$, as shown in Fig. 1(a), which also illustrates the very clean nature of the mass spectra obtained by ESMS. Figure 1(b) shows the comparison of the experimental and calculated isotopic mass distributions, which unequivocally identify the principal ion. Similar ES mass spectra were observed for all the products formed by the reaction of $Re(CO)_2(\eta^1\text{-}P\text{-}P)(\eta^2\text{-}P\text{-}P)X$ with MeI at room temperature. For the compounds $Re(CO)_2(\eta^1\text{-}apeMe)(\eta^2\text{-}ape)X$ (ape = $Ph_2AsCH_2CH_2PPh_2$; X = Cl, Br), in which the monodentate ape ligand is bound to the metal through phosphorus (^{31}P NMR spectroscopy), it was found that halide exchange occurs if the parent compound is refluxed with the methyl iodide in toluene, the ES mass spectrum showing peaks due to both $[Re(CO)_2(\eta^1\text{-}apeMe)(\eta^2\text{-}ape)X]^+$ and

TABLE 2. Electrospray mass spectra of cations of the types $[M(CO)_3(\eta^1\text{-P-PMe})(\eta^2\text{-P-P})]^+$ and $[M'(CO)_2(\eta^1\text{-P-PMe})(\eta^2\text{-P-P})X]^+$

Compound	Ions observed in ESMS after reaction with MeI (*m/z*) [a]	Daughter ions (*m/z*) CAD MS
$Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$	$[Cr(CO)_3(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})]^+$ (919)	$dpmMe^+$ (399)
	$dpmMe^+$ (399)	$Ph_2P{=}CH_2^+$ (199)
$Cr(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$	$[Cr(CO)_3(\eta^1\text{-apeMe})(\eta^2\text{-ape})]^+$ (1035)	
$Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$	$[Mo(CO)_3(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})]^+$ (965)	
$W(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$	$[W(CO)_3(\eta^1\text{-dpeMe})(\eta^2\text{-dpe})]^+$ (1079)	$dpeMe^+$ (413)
$Mn(CO)_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})Cl$	$[Mn(CO)_2(\eta^1\text{-dpeMe})(\eta^2\text{-dpe})Cl]^+$ (957)	
$Re(CO)_2(\eta^1\text{-dpm})(\eta^2\text{-dpm})Cl$	$[Re(CO)_2(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})Cl]^+$ (1061)	$dpmMe^+$ (399) $Ph_2P{=}CH_2^+$ (199) $PhP{\equiv}CH^+$ (121)
$Re(CO)_2(\eta^1\text{-dpm})(\eta^2\text{-dpm})Br$	$[Re(CO)_2(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})Br]^+$ (1105)	$dpmMe^+$ (399) $Ph_2P{=}CH_2^+$ (199) $PhP{\equiv}CH^+$ (121)
$Re(CO)_2(\eta^1\text{-dpm})(\eta^2\text{-dpe})Br$	$[Re(CO)_2(\eta^1\text{-dpmMe})(\eta^2\text{-dpe})Br]^+$ (1119)	
$dpmMe^+$ (399)		
	$dpmMe^+$ (399)	$Ph_2P{=}CH_2^+$ (199) $PhP{\equiv}CH^+$ (121)
$Re(CO)_2(\eta^1\text{-ape})(\eta^2\text{-ape})Cl$	$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})Cl]^+$ (1177)	
$Re(CO)_2(\eta^1\text{-ape})(\eta^2\text{-ape})Cl$ [b]	$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})Cl]^+$ (1177)	$apeMe^+$ (457)
	$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})I]^+$ (1269)	$Ph_2P{=}CH_2^+$ (199)
$Re(CO)_2(\eta^1\text{-ape})(\eta^2\text{-ape})Br$ [b]	$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})Br]^+$ (1221)	$apeMe^+$ (457)
	$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})I]^+$ (1269)	$Ph_2P{=}CH_2^+$ (199)
	$apeMe^+$ (457)	Ph_2As^+ (229)
		Ph_2P^+ (185)

[a] Strongest peak in the isotopic mass distribution. [b] Reacted with MeI under reflux in toluene.

$[Re(CO)_2(\eta^1\text{-apeMe})(\eta^2\text{-ape})I]^+$. However, no halide exchange was observed after reaction in dichloromethane at room temperature. In the ES mass spectrum of $[Mn(CO)_2(\eta^1\text{-dpeMe})(\eta^2\text{-dpe})Cl]^+$ (*m/z* 957) there is also a strong peak observed at *m/z* 907, assigned to $[Mn(CO)_2(dpe)_2]^+$, which was probably formed during the preparation of $Mn(CO)_2(\eta^1\text{-dpeMe})(\eta^2\text{-dpe})Cl$. The assignment was confirmed by comparison with the ES mass spectrum of an authentic sample of $[Mn(CO)_2(dpe)_2]^+$. Data for all these cations are given in Table 2.

The ES mass spectrometer used here [30] has the ability to select ions of a particular *m/z* and to pass these through a collision chamber, either in the presence or absence of a collision gas, and then into a second mass analyser. In each case, when the most abundant molecule ion (that is, an ion of a selected *m/z*, not the entire isotope distribution) of each phosphonium metal cation was passed into the second quadrupole mass filter without any collision gas, only the parent peak was observed. This shows that these ions are stable in the gas phase, with no metastable decomposition on the timescale of this experiment, which is of the order of 100 μs. However, in the presence of argon, collisionally activated decompositions (CAD) were observed. In all cases in which

TABLE 3. Electrospray mass spectra of $[M(CO)_5X]^-$ and $[M'(CO)_4X_2]^-$ anions

Compound	Principal ions (*m/z*) [a]
$NBu_4[Cr(CO)_5I]$	$[Cr(CO)_5I]^-$ (319)
$NBu_4[Mo(CO)_5I]$	$[Mo(CO)_5I]^-$ (365)
$NBu_4[W(CO)_5Cl]$	$[W(CO)_5Cl]^-$ (361)
$NBu_4[W(CO)_5Br]$	$[W(CO)_5Br]^-$ (405)
$NBu_4[W(CO)_5I]$	$[W(CO)_5I]^-$ (451)
$NBu_4[Mn(CO)_4BrI]$	$[Mn(CO)_4BrI]^-$ (373), $[Mn(CO)_4I_2]^-$ (421)
$NBu_4[Re(CO)_4Cl_2]$	$[Re(CO)_4Cl_2]^-$ (369)
$NBu_4[Re(CO)_4Br_2]$	$[Re(CO)_4Br_2]^-$ (459)
$NBu_4[Re(CO)_4ClBr]$	$[Re(CO)_4Br_2]^-$ (459), $[Re(CO)_4ClBr]^-$ (413), $[Re(CO)_4Cl_2]^-$ (369)
$NBu_4[Re(CO)_4ClI]$	$[Re(CO)_4I_2]^-$ (553), $[Re(CO)_4ClI]^-$ (461), $[Re(CO)_4Cl_2]^-$ (369)

[a] Strongest peak in the isotopic mass distribution.

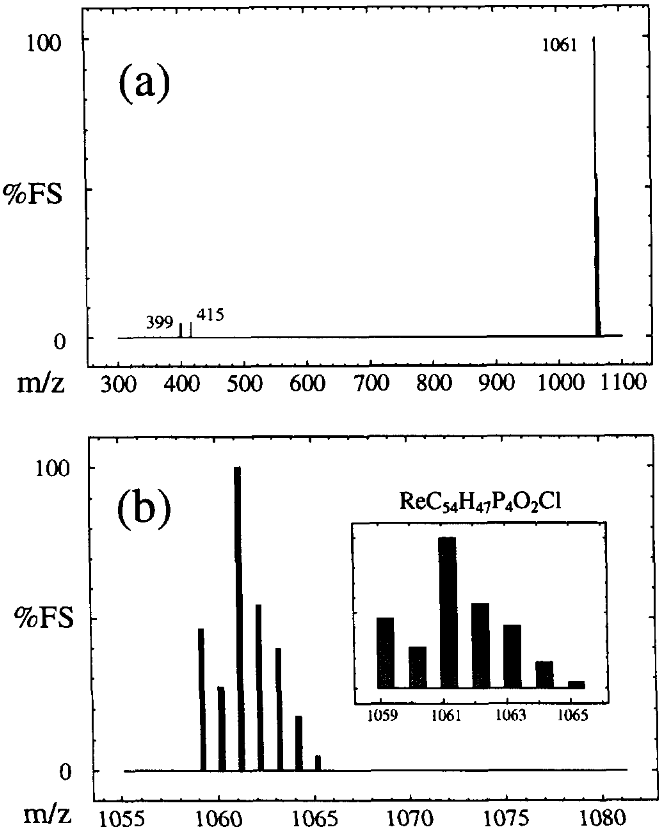

Fig. 1. (a) ES mass spectrum of $[Re(CO)_2(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})Cl]I$; (b) comparison between experimental and computed isotopic mass distribution for the principal ion.

fragmentation occurred, the major product was the methylated ligand P–PMe$^+$, together with its known [11] fragmentation products (Table 2). The ^{31}P NMR spectrum of the mixed ligand complex $Re(CO)_2(dpm)(dpe)Br$ (dpe = $Ph_2PCH_2CH_2PPh_2$) shows that it is the dpm ligand that is monodentate. This is confirmed by the CAD mass spectrum of the methylated derivative, which shows only the dpmMe$^+$ daughter ion and no dpeMe$^+$ daughter ion.

2.3. *Halocarbonyl anions of chromium, molybdenum and tungsten*

The negative ion electrospray mass spectrum of $NBu_4[Cr(CO)_5I]$ at low ion source energies (B1 = 30 V) gave the peak due to the principal ion $[Cr(CO)_5I]^-$ (m/z 319) together with another peak at m/z 291 which corresponds to loss of a carbonyl to give $[Cr(CO)_4I]^-$. The relative intensities of these peaks vary with the B1 voltage, the higher the voltage the smaller the relative intensity of the principal ion peak, thus confirming that the tetracarbonyl anion is formed by collisional activation in the vicinity of the ion source evaporation nozzle. At higher voltages (B1 = 60 V) additional peaks due to $[Cr(CO)_3I]^-$ (m/z 293) and $[Cr(CO)_2I]^-$ (m/z 265) are observed. Similar ES mass spectra have been obtained for other anions of this type, and data for typical examples are given in Table 3.

2.4. *Halocarbonyl anions of manganese(I) and rhenium(I)*

The halocarbonyl anions of manganese and rhenium of the types $[M(CO)_4X_2]^-$ gave their principal ions in the ES mass spectra at low B1 voltages. As in the previous cases, increasing the ion source voltage led to the appearance of ions deficient in carbonyl groups. The compounds were prepared by refluxing a solution of $M(CO)_5X$ with halide ion, and in the case of compounds containing two different halides, the ES mass spectra show that a mixture of products is produced. For example, the compound formulated as $NBu_4[Re(CO)_4ClBr]^-$ actually contains $[Re(CO)_4Cl_2]^-$ and $[Re(CO)_4Br_2]^-$ as well as the mixed halocarbonyl anion. Data for some typical examples are given in Table 3.

3. Discussion

The aim of this study was to demonstrate for the first time the systematic use of ESMS in metal carbonyl chemistry. We deliberately chose known compounds or others whose structures in solution can be verified by NMR spectroscopy in order to show that ESMS gives reliable information on the species present in the solution from which the ions are derived. In every case the principal ion with the expected m/z value was observed, usually as the base peak, and often as the only significant peak in the mass spectrum.

The observation of molecular ions for metal carbonyl compounds with conventional mass spectrometric methods is notoriously difficult, and fragmentation products, particularly those formed by loss of carbonyl ligands, usually dominate the mass spectra [1]. For the compounds studied in this paper, ESMS always gave the principal ions, although loss of carbonyl ligands was observed for the carbonyl rich anionic species.

Since we have shown that ESMS does indeed give accurate information about the species present in solution, it is obvious that combination of ESMS with spectroscopic or electrochemical methods will be very powerful in the identification of charged inorganic and organometallic species present in solution. We have already shown that ESMS is applicable in situations in which NMR spectroscopy is difficult or impossible, such as the identification of complex mixtures of rapidly exchanging compounds, *e.g.* copper phosphine cations

[31], and paramagnetic, 17-electron species such as *trans*-$[Cr(CO)_2(dpe)_2]^+$ [9].

We believe that as the relevant instrumentation becomes more commonly available, the ESMS technique will emerge as a powerful method for the study of solutions of a wide range of charged inorganic and organometallic systems. Not only does the technique provide a method of obtaining mass spectra from a solution, but it also allows the mass spectra of charged species to be observed routinely for the first time. It is extremely easy to use and the only requirement is that the compound is soluble and stable in a suitable solvent. The ion source temperature is typically maintained at about 55–60°C, and so there are no stringent requirements of thermal stability of the compounds under investigation.

4. Experimental details

The compounds $M(CO)_2(P\text{-}P)_2$ [12], $[M(CO)_5X]^-$ [24], $[M'(CO)_4X_2]^-$ [25], $M(CO)_3(\eta^1\text{-}P\text{-}P)(\eta^2\text{-}P\text{-}P)$ and $M'(CO)_2(\eta^1\text{-}P\text{-}P)(\eta^2\text{-}P\text{-}P)X$ (P–P = dpm, dpe) [19,20,23] were prepared by literature methods. $Mn(CO)_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})Cl$ was prepared by the same method [23]. The complexes of the latter type containing ape were prepared similarly and ^{31}P NMR spectroscopy in $CDCl_3$ (Bruker AM 300) showed the η^1-ape ligand to be phosphorus bound to the metal. The mixed ligand complex $Re(CO)_2(\eta^1\text{-dpm})(\eta^2\text{-dpe})Br$ was prepared by treating $Re(CO)_3(dpe)Br$ with an equimolar quantity of dpm. The ^{31}P NMR spectrum confirmed that the dpe ligand remained bidentate to the metal. The pendant phosphines (or arsines) were converted into the corresponding methylphosphonium group by reaction with methyl iodide overnight in dichloromethane at room temperature or, for the ape derivatives, in toluene under reflux. The solvent was removed under vacuum and the solids recrystallized from dichloromethane/hexane.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer [30] using a water/methanol/acetic acid mobile phase. The cationic compounds were dissolved in dichloromethane (2 mM) and this solution was then diluted 1:10 with either dichloromethane or methanol. Acetonitrile solutions (0.2 mM) were used for negative ion ESMS as they give a more stable ion jet. Halogen exchange was observed in the negative ion mode when dichloromethane was present in the solvent. The diluted solution was injected directly into the spectrometer via a Rheodyne injector using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 $\mu l\ min^{-1}$. The voltage on the first skimming electrode (B1) was varied between 70 V and the minimum necessary to maintain a stable ion jet. This value varied from time to time, but was typically about 30 V in the positive ion mode and as low as 20 V in the negative ion mode. CAD mass spectra were generated by admitting argon to the collision cell to a pressure that gave a 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

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