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Characterization of bis(diphenylphosphino)methane and bis(diphenylphosphinomethyl)phenylphosphine complexes of platinum(II) and palladium(II) by fast-atom-bombardment mass spectrometry

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Abstract

The positive fast-atom-bombardment (FAB) mass spectra of $[M(dppm)X_2]$ (dppm = $Ph_2PCH_2PPh_2$; M = Pt, X = Cl, Br or I; M = Pd, X = Cl), $[M(dpmp)X_2]$ (dpmp = $Ph_2PCH_2PPhCH_2PPh_2$; M = Pt, X = Cl, Br, I or CH_3; M = Pd, X = Cl), and $Pt(dppm)_2X_2$ (X = Cl, Br, I or PF_6) in a 3-nitrobenzyl alcohol matrix, together with electron-impact mass spectra for PPh_3, dppm and dpmp, are reported. The use of other matrices and different ionization techniques is also discussed. The complexes exhibit fragmentation pathways similar to those of the free ligands, and the wide utility of FAB mass spectrometry for the identification of monomeric platinum and palladium phosphine complexes and salts is clearly demonstrated.

Introduction

Fast-atom-bombardment mass spectrometry (FAB-MS), since its development by Barber and coworkers [1,2], has established itself as a useful technique for the analysis of compounds not amenable to electron-impact (EI) or chemical ionization (CI) mass spectrometry. A prerequisite of FAB-MS is that the sample be dissolved in a matrix liquid, the nature of which plays an important rôle in the quality of spectra obtained. Although glycerol is probably the most widely used matrix, several others, each best suited to a particular class of compound, have been reported [3]. Over the last six years, FAB-MS has been applied to the study of different classes of inorganic (including organometallic) and coordination compounds [4–6], and the co-ordination compounds of platinum and palladium have received considerable attention. Groves and coworkers [7] have obtained the FAB-MS of $[M(PPh_3)_4]$ (M = Pt or Pd), but in neither case was a molecular ion observed (although in the

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spectrum of the platinum complex, the binuclear species $[Pt_2(PPh_3)_n]$ ($n = 2$–4) were detected). Some tetraalkylammonium salts of platinum and palladium have been studied by negative and positive FAB-MS [8]; molecular ions for these salts were observed only in the negative mode.

We report here the FAB spectra of some bis(diphenylphosphino)methane (dppm; $Ph_2PCH_2PPh_2$) and bis(diphenylphosphinomethyl)phenylphosphine (dpmp; $Ph_2PCH_2PPhCH_2PPh_2$) complexes of platinum(II) and palladium(II), together with the EI spectra of the free ligands. The EI mass spectrum of dppm has been studied previously by Colton and Porter [9].

Experimental

Mass spectra were obtained using a Kratos Analytical Ltd MS80RF double focusing mass spectrometer, interfaced to a Kratos DS55M data system. Samples were evaporated from a heatable direct insertion probe with an ion source temperature of 250 °C. A 4 kV accelerating voltage, 70 eV electron energy and trap current of 100 μA were used, the resolution being a nominal 1000. By linking the magnetic field, B, and the electrostatic analyzer voltage, E, such that a constant B/E ratio was maintained during scans (B/E scans), spectra showing daughter ions derived from decompositions occurring in the first field-free region of the MS80RF mass spectrometer provided confirmation of fragmentation pathways.

The FAB spectra were obtained with a dedicated ion source (Kratos) fitted with a FAB11 atom gun and B50 power supply (Ion Tech Ltd). Xenon ('research' grade; BOC Ltd) at a flow rate of 0.5 $cm^3\ min^{-1}$ was used as the bombarding gas, with atom gun energies of 6–8 kV and ion currents of between 30 and 40 μA. Samples were dissolved in the matrix liquid, with or without co-solvent, and spread over a 2×10 mm stainless-steel platform mounted at the end of a direct insertion probe. The source was operated at room temperature at an accelerating voltage of 4 kV and a resolution of between 1000 and 3000. The mass scan time was 30 s $decade^{-1}$ for FAB spectra, and 3 s $decade^{-1}$ for EI and CI spectra.

The ligand dpmp was prepared and purified as described elsewhere [10]; dppm (ex BDH) was purified by recrystallization from methanol. The complexes $[Pd(dppm)Cl_2]$ and $[Pt(dppm)X_2]$ (X = Cl, Br or I) were prepared by established methods [11,12]. The platinum(II) complexes were then used to prepare the complexes $Pt(dppm)_2X_2$ (X = Cl, Br, I, PF_6 or BPh_4) [13]. Literature methods [14,15] were used to prepare the complexes $[Pt(dpmp)Cl_2]$, $[Pt(dpmp)(CH_3)_2]$ and $[Pd(dpmp)Cl_2]$, while $[Pt(dpmp)Br_2]$ was prepared by treatment of $[Pt(cod)Br_2]$ (cod = cycloocta-1,5-diene) with dpmp dissolved in dichloromethane [16]. $[Pt(dpmp)I_2]$ was prepared by treating a solution of $[Pt(dpmp)Cl_2]$ in propanone with sodium iodide [16].

The matrix liquid 3-nitrobenzyl alcohol (Fluka AG) was used without further purification.

Results and discussion

Mass spectra of the free ligands, PPh_3, dppm and dpmp

The electron impact mass spectrum of dppm is shown in Fig. 1(a); the molecular ion was observed, and the base peak at m/z 262 was identified as the triphenyl-

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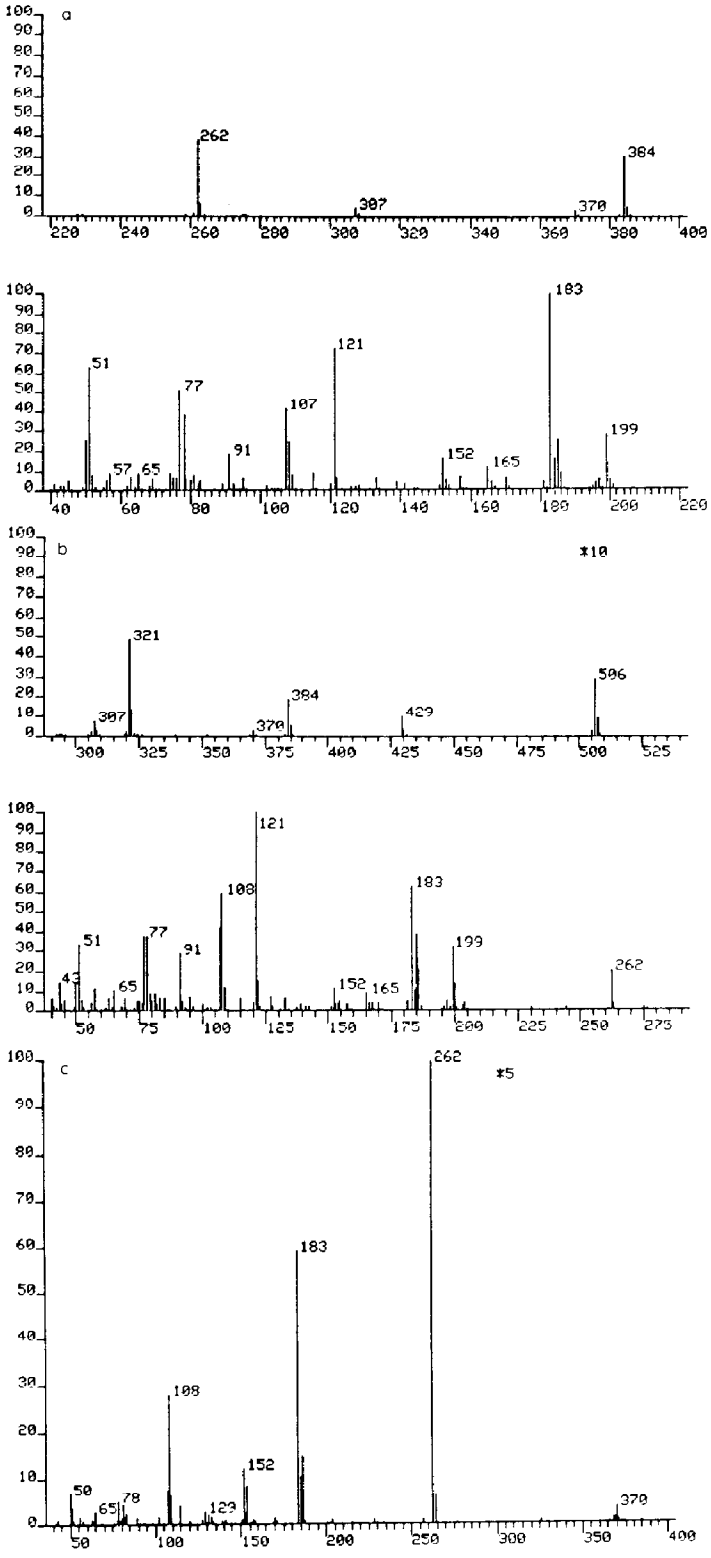


Fig. 1. The EI (70 eV) mass spectra of (a) dppm, (b) dpmp, and (c) triphenylphosphine.

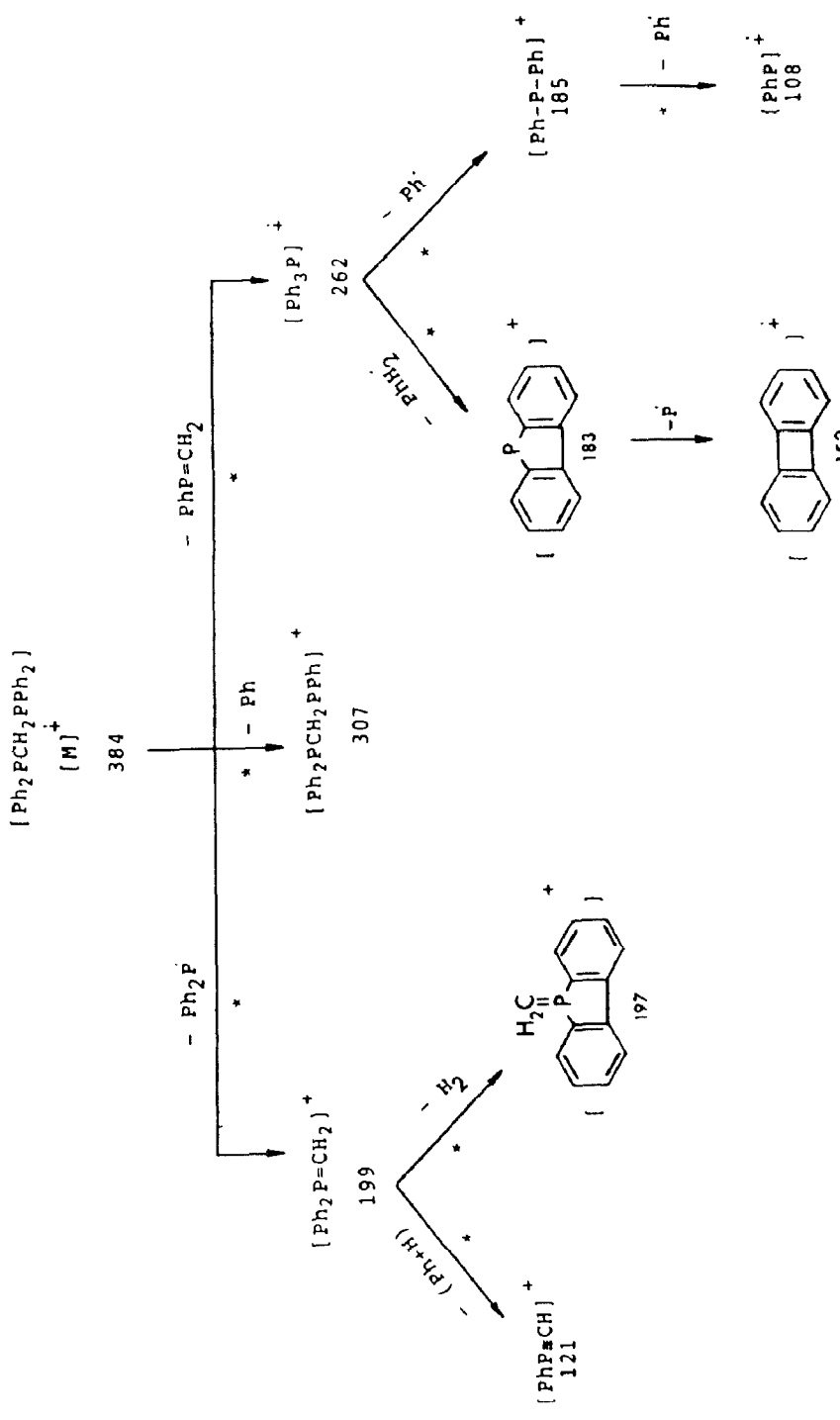


Fig. 2. The key fragmentation pathways for dppm; the asterisk denotes those pathways which were confirmed by metastable peaks.

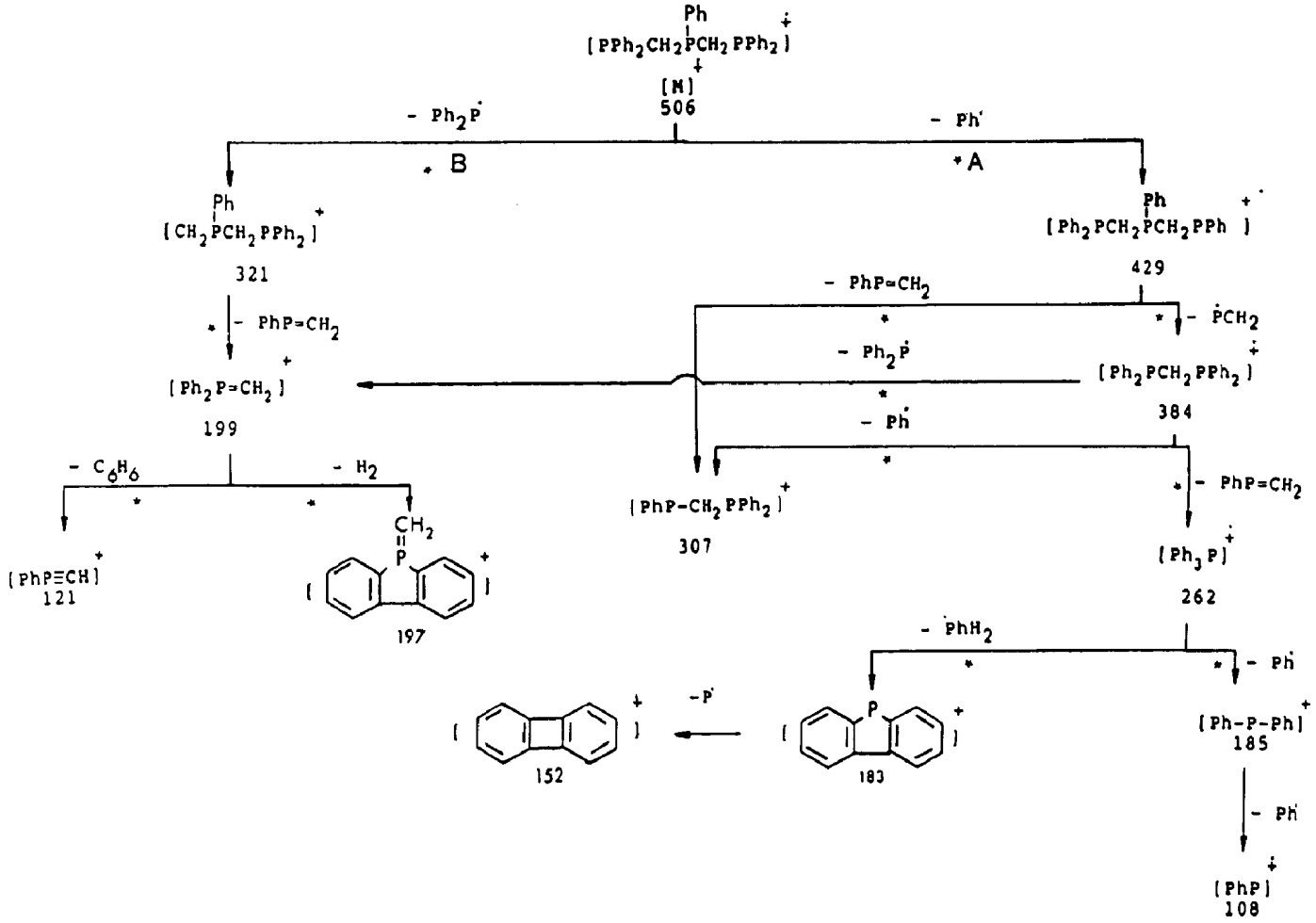


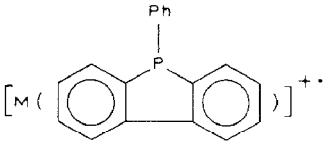
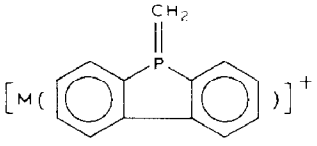
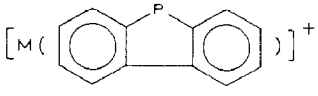
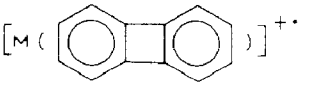
Fig. 3. The key fragmentation pathways for dpmp; the asterisk denotes those pathways which were confirmed by metastable peaks.

phosphine radical cation $[PPh_3]^{+\cdot}$. Metastable studies showed that this fragment ion was produced directly from the molecular ion, involving a 1,3-phenyl migration. Further fragmentations of this radical cation were similar to those shown in the EI mass spectrum of triphenylphosphine, Fig. 1(c) {cf. [17]}. Other major fragments and their formation pathways, again confirmed by metastable transitions, are summarized in Fig. 2.

The EI spectrum of dppm showed a very weak ion at m/z 370, which Colton and Porter [9] ascribed to the loss of methylene from the molecular ion. The elimination of methylene from such a molecule is highly unlikely, and we could not detect the metastable transition from the molecular ion. We thus postulate that this $[Ph_2PPPh_2]^+$ ion results from the combination of two diphenylphosphine ions when the sample pressure within the ion source is particularly high. Support for this

Table 1

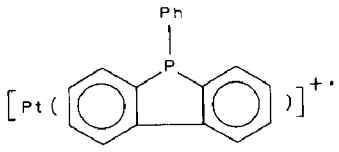
Major metal-containing fragment ions in the FAB mass spectra of $[M(dppm)X_2]$ (M = Pt or Pd) complexes

Fragment ion	m/z [a] and % abundances [b]			
	M = Pd	M = Pt		
	X = Cl	Cl	Br	I
$[M(dppm)X_2]^{+\cdot}$	–	649(7)	–	–
$[M(dppm)X]^+$	525(61.7)	614(100)	658(100)	706(100)
$[M(dppm)]^{+\cdot}$	490(18.3)	579(6)	579(20.2)	579(14.7)
$[M(PhPCH_2PPh_2)]^+$	413(21.7)	502(7)	502(18.3)	502(20.6)
$[M(PhPPPh_2)]^+$	399(35)	–	–	–
$[M(Ph_3P)]^{+\cdot}$	368(45)	457(6)	–	457(7.4)
	–	455(7)	–	455(7.4)
$[M(Ph_2P{=}CH_2)]^+$	305(100)	394(9)	394(1.2)	394(17.6)
	–	392(6)	392(1.1)	392(23.5)
$[M(Ph_2P)]^+$	291(80)	380(7)	380(1.1)	380(26.5)
	–	378(11)	378(2.6)	378(26.5)
	–	347(9)	–	347(26)

[a] Nominal mass, using the lowest mass isotopes of each element. [b] Relative intensities are normalized to the most intense metal-containing fragment ion, and given in parentheses.

Table 2

Major metal-containing fragment ions in the FAB mass spectra of $Pt(dppm)_2X_2$ salts

Fragment ion	m/z [a] and % abundances [b]			
	X = Cl	Br	I	PF_6
$[Pt(dppm)_2X_2]^{+\cdot}$	–	–	–	–
$[Pt(dppm)_2X]^+$	998(6)	1042(29.9)	1090(100)	1108(32)
$[Pt(dppm)_2]^{+\cdot}$	963(100)	963(100)	963(48)	963(100)
$[Pt(L)(PhPCH_2PPh_2)]^+$ [c]	886(14)	886(20.7)	886(20)	886(19)
$[Pt(L)(PhP{=}CH_2)]^+$ [c]	778(18)	778(13.8)	778(15.5)	778(17.5)
$[Pt(L)(Ph_2P)]^+$ [c]	764(9)	764(10.3)	764(9)	764(11)
$[Pt(dppm)X]^+$	614(33)	658(80.5)	706(79)	–
$[Pt(dppm)]^{+\cdot}$	579(2)	579(5.7)	579(9)	579(9)
$[Pt(Ph_2PCH_2PPh)]^+$	502(11)	502(24.1)	502(23)	502(1.2)
$[Pt(Ph_3P)]^{+\cdot}$	457(19)	457(34.5)	457(37)	–
	455(23)	445(44.8)	455(42)	–

[a] Nominal mass, using the lowest mass isotopes of each element. [b] Relative intensities are normalized to the most intense metal-containing fragment ion, and given in parentheses. [c] L = $Ph_2PCH_2PPh_2$.

suggestion can be seen in the mass spectrum of triphenylphosphine {Fig. 1(c)}, which exhibits a similar (but previously unreported) ion at m/z 370, as well as $[PPh_2]^+$ at m/z 185. No ion at m/z 370 was detected under CI or FAB conditions for either dppm or dpmp.

The electron-impact mass spectrum of dpmp {Fig. 1(b)}, which is the tridentate analogue of dppm, was also studied. The fragmentation pattern of this ligand, confirmed by metastable transitions, comprised two major pathways each commencing from the molecular ion (Fig. 3). In pathway A, the molecular ion loses a phenyl radical to give the $[Ph_2PCH_2P(Ph)CH_2PPh]^+$ fragment ion (m/z 429), which then loses $[P{=}CH_2]^{\cdot}$ to give the molecular radical cation of the dppm ligand, $[Ph_2PCH_2PPh_2]^{+\cdot}$ (m/z 384): this then shows the same fragmentation pathways as shown by dppm (Fig. 2). In pathway B, the molecular ion loses the diphenylphosphine radical to give the $[CH_2P(Ph)CH_2PPh_2]^+$ fragment ion at m/z 321, which then ejects the $PhP{=}CH_2$ neutral molecule to give the fragment ion $[Ph_2P{=}CH_2]^+$ at m/z 199. The latter ion was subjected to parallel loss of either dihydrogen or benzene molecules to give fragment ions at m/z 197 or 121, respectively.

FAB mass spectra of some dppm complexes of platinum(II) and palladium(II)

The coordination complexes of dppm with platinum(II) and palladium(II) (Tables 1, 2) were studied under three different ionization techniques (EI, CI and desorption chemical ionization, DCI) before being studied by FAB-MS. A weak DCI spectrum was obtained for $[Pt(dppm)Cl_2]$ {Fig. 4(b)}; no other complex gave useful data.

The FAB mass spectra of complexes $[Pt(dppm)X_2]$ (X = Cl, Br or I), $Pt(dppm)_2X_2$ (X = Cl, Br, I or PF_6) and $[Pd(dppm)Cl_2]$ were obtained using 3-nitrobenzyl alcohol

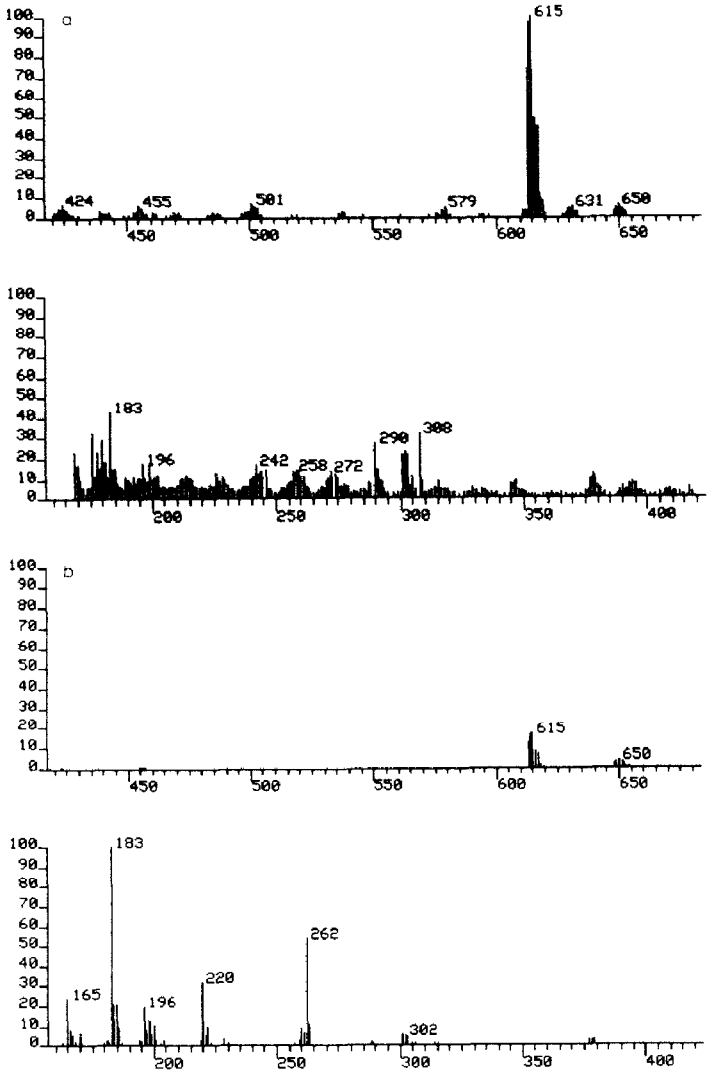


Fig. 4. (a) The positive FAB mass spectrum of $[Pt(dppm)Cl_2]$. (b) The DCI mass spectrum of $[Pt(dppm)Cl_2]$, at a sample temperature of 350 °C and using NH_3 reagent gas.

as a matrix. Only $[Pt(dppm)Cl_2]$ exhibits a molecular ion {Fig. 4(a)}; the remaining complexes give ions corresponding to the loss of one halogen atom, $[M - X]^+$. This ion is the base peak of the spectrum for each of the complexes except for $[Pd(dppm)Cl_2]$, where the $[Pd(Ph_2P{=}CH_2)]^+$ ion is the base peak (Fig. 5).

The fragment ion $[M - X]^+$ loses a second halide, X, giving the $[M - 2X]^{+\cdot}$ radical cation, of low intensity; further fragmentation follows a pathway similar to that of the free ligand.

The complexes $Pt(dppm)_2X_2$ gave more intense spectra (Fig. 6), exhibiting fragmentation pathways similar to those of $[M(dppm)X_2]$ (M = Pt or Pd). Moreover, they showed an additional pathway due to the loss of a ligand radical from the $[M - X]^+$ fragment ion, giving rise to $[M - X - dppm]^+$ (Fig. 7). All complexes exhibited the fragment ion $[Pt(dppm)_2X]^+$ (X = Cl, Br, I or PF_6), irrespective of the nature of X. Recently, we [13] proposed that the halide salts $Pt(dppm)_2X_2$ (X = Cl,

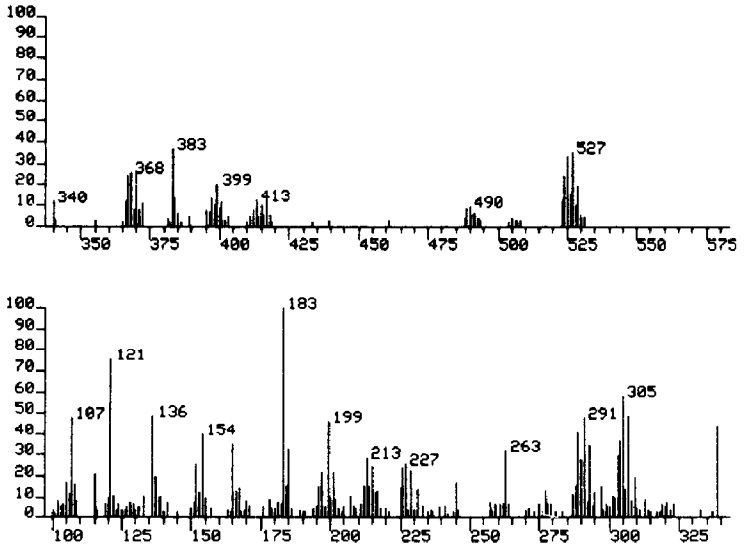


Fig. 5. The positive FAB mass spectrum of $[Pd(dppm)Cl_2]$.

Br or I) formed the five-coordinate cation $[Pt(dppm)_2X]^+$ in solution, whereas $[Pt(dppm)_2][PF_6]_2$ formed the square-planar cation $[Pt(dppm)_2]^{2+}$. We had hoped that a FAB-MS study would provide further data on this unusual situation but, unfortunately, the FAB mass spectra are unable to distinguish whether $[Pt(dppm)_2X]^+$ exists as a five-coordinate adduct $[Pt(dppm)_2X]^+$ or is present as the contact ionic pair, $\{Pt(dppm)_2\}^{2+}/X^-$.

FAB mass spectra of some dpmp complexes of platinum(II) and palladium(II)

The coordination complexes of dpmp with platinum(II) and palladium(II) (Table 3) were studied under three different ionization techniques (EI, CI and DCI) before being studied by FAB-MS; no useful data were obtained.

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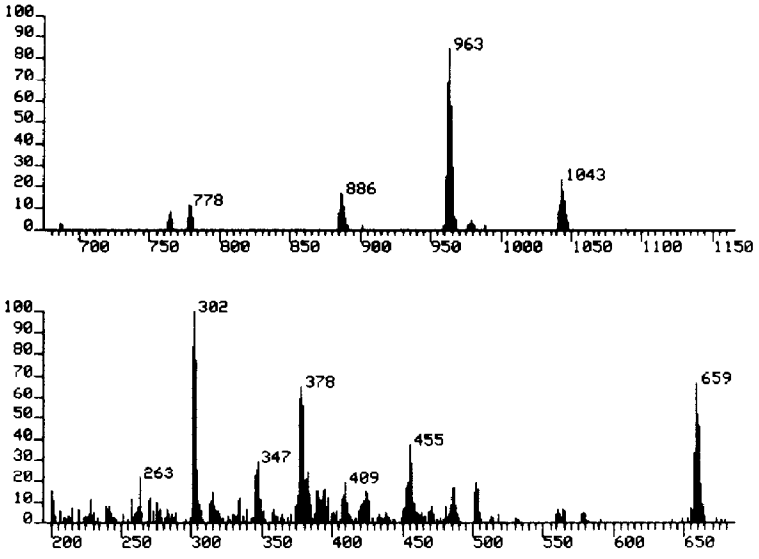


Fig. 6. The positive FAB mass spectrum of $Pt(dppm)_2Br_2$.

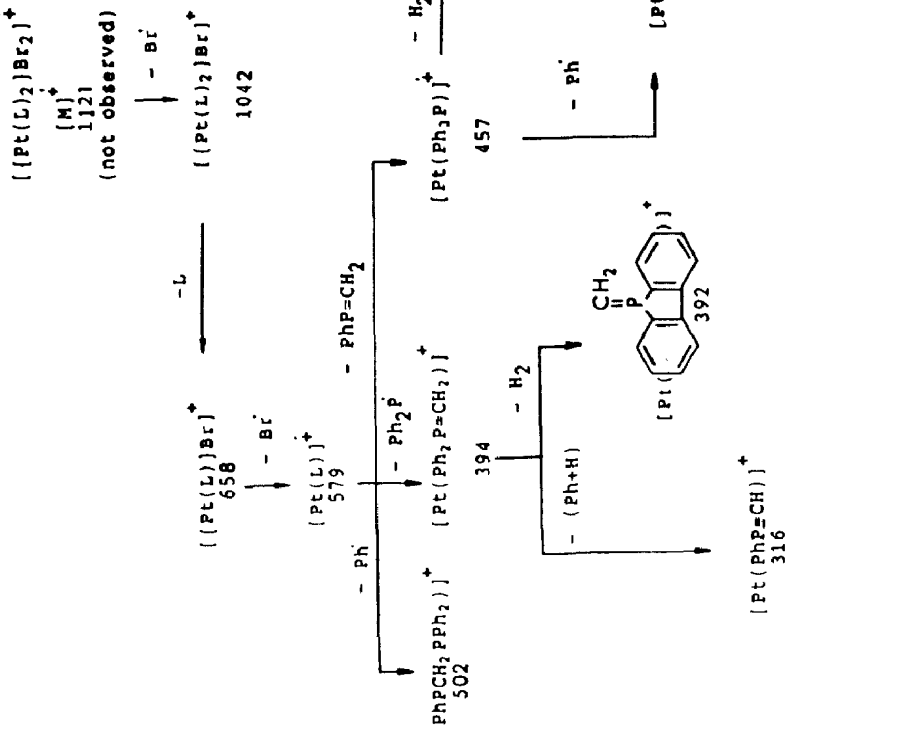
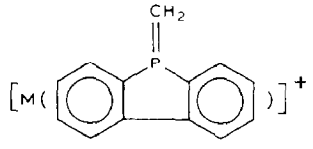
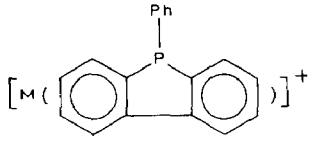
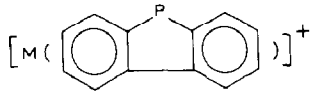


Fig. 7. The proposed key fragmentation pathways for $Pt(dppm)_2Br_2$ ($L = Ph_2PCH_2PPh_2$).

Table 3

Major metal-containing fragment ions in the FAB mass spectra of $[M(dpmp)X_2]$ (M = Pt or Pd) complexes

Fragment ion	*m/z* [a] and % abundances [b]				
	M = Pd	M = Pt			
	X = Cl	Cl	Br	I	CH_3
$[M(dpmp)X_2]^{+\cdot}$	–	–	–	–	–
$[M(dpmp)X]^+$	647(49)	736(100)	780(100)	828(100)	716(100)
$[M(dpmp)]^{+\cdot}$	612(11)	701(27)	701(18)	701(9.6)	701(34)
$[M(Ph_2PCH_2PPhCH_2)]^+$	427(10)	–	516(5)	516(3.2)	516(4)
$[M(Ph_2P{=}CH_2)]^+$	305(95)	394(19)	394(17)	394(9.6)	394(26)
	–	392(22)	392(17)	392(9.6)	392(7)
$[M(dppm)X]^+$	525(11)	614(11.7)	658(12)	706(7.4)	594(6)
$[M(dppm)]^{+\cdot}$	490(28)	579(8)	579(6)	579(2.1)	579(4)
$[M(Ph_2PCH_2PPh)]^+$	413(40)	502(20)	502(17.5)	502(10.6)	502(14)
$[M(Ph_3P)]^{+\cdot}$	368(42)	457(42)	457(8)	457(2.1)	457(6)
	–	455(15.6)	455(11)	455(2.8)	455(13)
$[M(Ph_2P)]^+$	291(100)	380(11)	380(10.5)	380(9.6)	380(6.8)
	–	378(31)	378(19)	378(7.4)	378(26)

[a] Nominal mass, using the lowest mass isotopes of each element. [b] Relative intensities are normalized to the most intense metal-containing fragment ion, and given in parentheses.

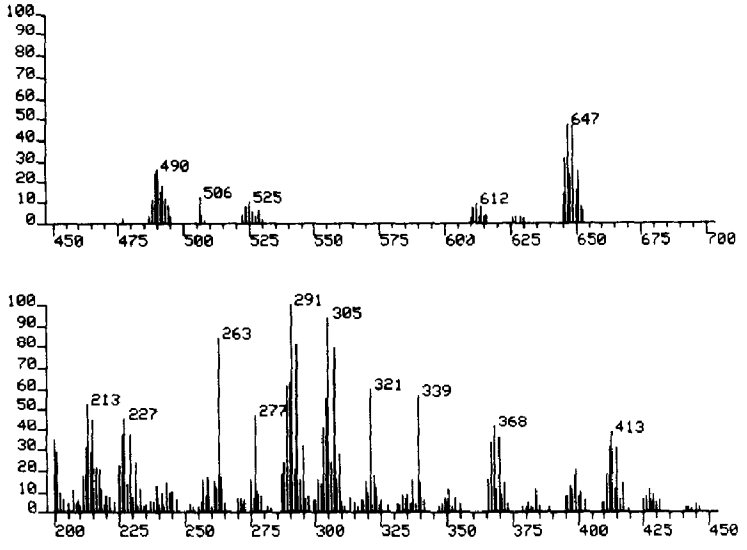


Fig. 8. The positive FAB mass spectrum of $[Pd(dpmp)Cl_2]$.

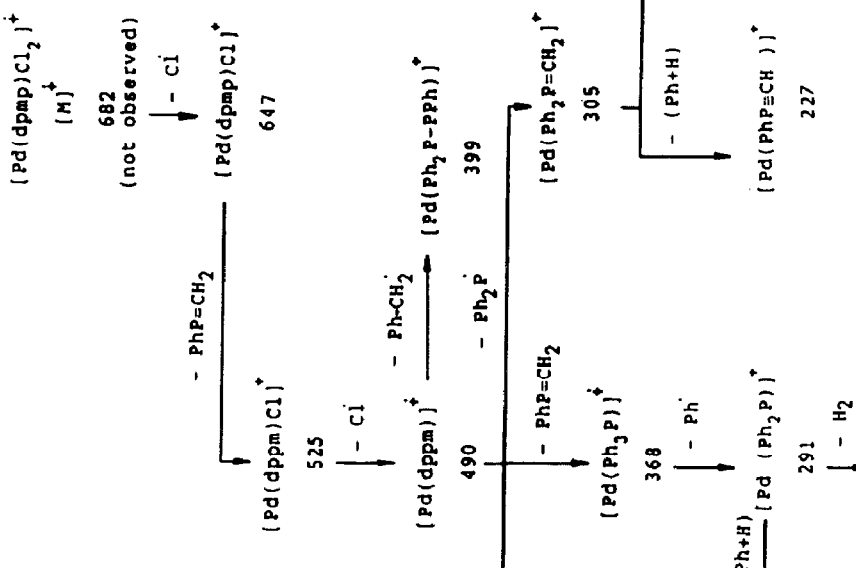


Fig. 9. The proposed key fragmentation pathways of [Pd(dpmp)Cl_2].

The mass spectra of the complexes $[Pt(dpmp)X_2]$ (X = Cl, Br, I or CH_3) and $[Pd(dpmp)Cl_2]$ were obtained using 3-nitrobenzyl alcohol. No complex gave a molecular ion, but all showed $[M - X]^+$ as the highest mass fragment ion (Fig. 8). Two fragmentation pathways were apparent, the first was for the $[M - X]^+$ fragment ion to lose a second ligand (X) to give the $[M - 2X]^{+\cdot}$ ion. The second pathway was for the $[M - X]^+$ ion to eject a neutral molecule $[PhP{=}CH_2]$ to give

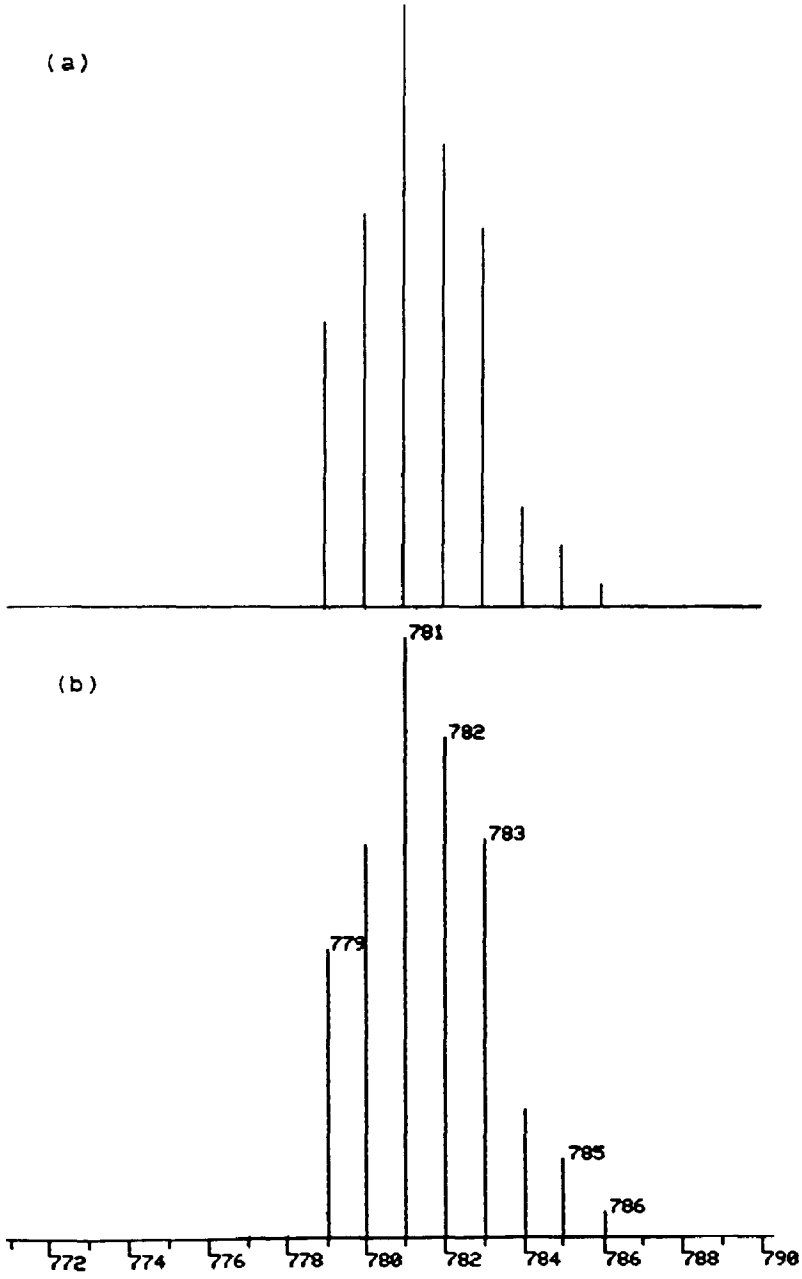


Fig. 10. (a) A computer simulation of, and (b) the experimental isotopic pattern for, $[Pt(dpmp)Br_2]$ in the $[M - Br]^+$ ion region.

the $[M - X - (PhP{=}CH_2)]^+$ ion and then to lose a second ligand (X) to give either the $[Pt(dppm)]^{+\cdot}$ or $[Pd(dppm)]^{+\cdot}$ fragment ion. The ions $[M - 2X]^{+\cdot}$ and $[Pt(dppm)]^{+\cdot}$ or $[Pd(dppm)]^{+\cdot}$ then followed fragmentation pathways similar to those shown by the free ligands dpmp and dppm respectively (except, of course, that the fragment ions were coordinated to a metal atom). The fragmentation pathways of $[Pd(dpmp)Cl_2]$ (Fig. 9) are typical of the fragmentation pathways exhibited by all of these complexes.

By comparing the ion intensities of the ions produced from the free ligands and their metal-containing analogues, it can be seen that the metal atom has an influence upon the stability of the ions produced. Platinum and palladium destabilized the dppm fragment in the spectra of $[Pt(dpmp)Cl_2]$ and $[Pd(dppm)Cl_2]$ (m/z 579 and 490, respectively), whilst palladium stabilized the fragment ion $[Ph_2P{=}CH_2]^+$ and $[PPh_2]^+$ (m/z 305 and 291) in the spectrum of $[Pd(dpmp)Cl_2]$ (Fig. 9).

As the matrix liquid is one of the most important variables in FAB-MS, several were used to study these complexes: glycerol, sulfolane, tetraglyme, 18-crown-6/tetraglyme (9/1), and hexamethylphosphoramide. However, 3-nitrobenzylalcohol was found to be the most suitable, the only disadvantage of this matrix being that it occasionally donated an oxygen atom to some fragment ions of the spectra. Comparison of the DCI and FAB spectra for the complex $[Pt(dppm)Cl_2]$ (Fig. 4) shows no additional ions between $M^{+\cdot}$ and $[M - Cl]^+$ in the DCI spectrum, whereas the FAB spectrum shows a fragment at m/z 631 due to the addition of an oxygen atom to the fragment ion $[M - Cl]^+$ at m/z 615.

Conclusions

In each of the complexes and salts examined, either the molecular ion, $M^{+\cdot}$, or the molecular ion minus one halide ion, $[M - X]^+$, was identified. No evidence for oligomerization was observed, and excellent agreement between the experimental data for, and computer simulations of, the isotopic patterns for these complexes in the regions of the molecular ion and/or $[M - X]^+$ fragment ion were obtained (e.g. Fig. 10). This provides an excellent basis for the confident identification of other involatile, partially soluble and/or amorphous complexes upon the basis of their observed FAB spectra.

Acknowledgements

We thank Miss F.J. Walker for donation of the complexes $Pt(dppm)_2X_2$ (X = Cl, Br, I and PF_6), and Johnson-Matthey for the loan of salts of platinum and palladium. Two of us (K.A.A. and A.A.S.) are indebted to the Iraqi Government for the award of research scholarships.

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