Coordination complexes and organometallic complexes of palladium and platinum with polydentate ligands containing pyrazole groups and related ligands: an electrospray mass spectrometric study

Allan J. Canty and Peter R. Traill
Chemistry Department, University of Tasmania, Hobart 7001 (Australia)

Ray Colton* and Ian M. Thomas
Chemistry Department, La Trobe University, Bundoora 3083 (Australia)

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Abstract

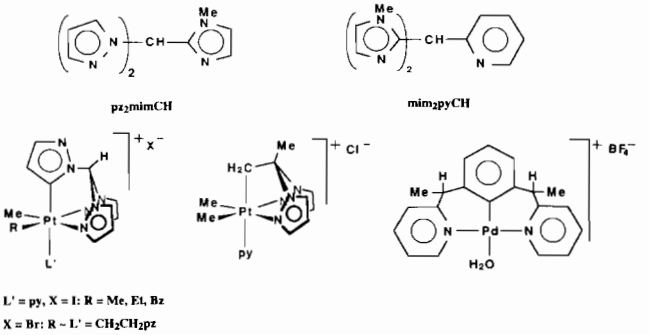
Electrospray mass spectra have been obtained from methanol solution for a wide variety of organometallic compounds of palladium(IV,II) and platinum(IV) containing polydentate nitrogen donor ligands. In almost every case the intact ion was observed as the base peak, and often as the only peak, at low ion source energies emphasising the very soft nature of the transfer of ions from solution to the gas phase. Daughter ions were generated either by collisional activated decompositions involving solvent molecules within the ion source as the source energy was increased, or alternatively by tandem mass spectrometry using argon as the collision gas. The palladium(IV) complexes all undergo very facile reductive elimination of two methyl groups, as expected for palladium(IV) complexes. In contrast, platinum(IV) compounds retain their organo groups at low ion source energies.

Introduction

Electrospray mass spectrometry (ESMS) is a new technique which allows pre-existing ions in solution to be very gently transferred to the gas phase with minimal fragmentation, followed by conventional mass spectrometry. The ES technique has been developed mainly by Fenn and co-workers [1–3] and to date its most spectacular successes have been in the area of mass spectrometry of large bio-molecules [4, 5].

We have been exploring the application of ESMS to inorganic and organometallic systems [6–11]. In the cases of non-labile species, for example phosphonium salts and cations such as $[(P\text{-}P)Pt(S_2CNEt_2)]^+$ (P-P = diphosphine), the intact ions are usually observed without difficulty [6–8]. However, with labile complexes, daughter ions formed by loss of one or more ligands may be observed as well as the intact ions. Interestingly, in cationic or anionic systems where ligands exchange rapidly on the NMR timescale at room temperature, the ESMS technique allows observation of the individual species at room temperature and provides a viable alternative to low temperature NMR studies for their characterisation. Examples of exchanging systems to which this technique has already been applied include cationic mixed phosphine mercury(II) complexes [9] and mixed tris(dithiophosphato)zinc(II) anions [10].

In this paper we examine the ES mass spectra of a representative selection of organopalladium(II,IV) and platinum(IV) complexes and related palladium(II) complex ions, with polydentate nitrogen based ligands [11–18] to illustrate the applicability of the ESMS method to palladium and platinum chemistry. The nitrogen ligands studied include tris(pyrazol-1-yl)-alkanes (pz_3CR, R = H, Me), tris(pyridin-2-yl)methane (py_3CH) and the ligands shown in Scheme 1. Organic groups attached to the metal atom include methyl,



Scheme 1.

*Author to whom correspondence should be addressed.

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ethyl, 2-propenyl, η^3-propenyl, phenyl and the intramolecular coordination groups shown in Scheme 1.

Results and discussion

Throughout this paper peaks in the ES mass spectra will be identified by the most intense *m/z* value within the isotopic mass distribution. In all cases there was good agreement between the experimental and calculated isotopic mass distributions.

Palladium(IV) complexes

Data for all palladium(IV) compounds are given in Table 1.

Figure 1 shows the positive ion ES mass spectrum of $[Me_2(C_3H_5)Pd(mim_2pyCH)]I$ at a low ion source energy (25 V on the first skimmer, B1). The three peaks correspond to the intact ion $[Me_2(C_3H_5)Pd(mim_2pyCH)]^+$ (*m/z* 430), $[(C_3H_5)Pd(mim_2pyCH)]^+$ (*m/z* 400) formed by loss of Me_2 and $[MePd(mim_2pyCH)]^+$ (*m/z* 374) formed by loss of $(Me + C_3H_5)$. This amount of ligand loss at low ion source energies is unusual in ES mass spectra and reflects the known facile reductive elimination from organopalladium(IV) complexes [19]. Nevertheless, the general lack of fragmentation and the signal to noise ratio of this spectrum are typical for the spectra reported in this paper.

Further fragmentation of the intact ion can be induced by increasing the B1 voltage which causes collisionally activated decompositions with solvent molecules within the ion source where the pressure is close to atmospheric. Using B1 voltages between 25 and 50 V no new peaks appear in the ES mass spectrum, although the relative intensity of the peak due to the intact ion decreases. Figure 2 shows the effect of varying the B1 voltage from 40 V to 100 V. At B1 = 80 V (Fig. 2(b)) the peak due to the intact ion has disappeared and that due to $[(C_3H_5)Pd(mim_2pyCH)]^+$ is the base peak. In addition, new daughter ions occur at *m/z* 359, assigned to $[Pd(mim_2pyCH)]^+$, and (not shown in Fig. 2) 254 and 252 (without the characteristic palladium isotope pattern) assigned to $[(mim_2pyCH_2)]^+$ and $[(mim_2pyC)]^+$, respectively. The protonated ligand presumably arises from reaction in the gas phase between dissociated ligand and the acetic acid from the mobile phase (see 'Experimental'). At a B1 voltage of 100 V the fragmentation is even more pronounced (Fig. 2(c)). An interesting feature of these ES mass spectra is the demonstration of the well known strong affinity between palladium and allyl ligands. As will be seen in other mass spectra in this paper, complete loss of alkyl groups occurs at B1 voltages much less than 100 V. Even at low ion source energies, the preferential loss of Me_2 rather than $(Me + C_3H_5)$ from the parent ion is obvious (Fig. 1).

The compounds $[Me_3Pd(mim_2pyCH)]I$ and $[Me_2EtPd(mim_2pyCH)]I$ show generally similar behaviour except that at B1 = 100 V no peaks due to palladium species are observed above *m/z* 359, assigned to $[Pd(mim_2pyCH)]^+$. Although triorganopalladium(IV) complexes generally undergo facile reductive elimination [19], the complexes of mim_2pyCH are stable in solution up to 60 °C [14]. The detection of reductive elimination by ESMS, and the extent of reductive elimination, thus provides a new method for probing such processes.

The positive ion ES mass spectrum of $[Me_3Pd(pz_3CH)]BF_4$ at low ion source energy (B1 = 25 V) is dominated by the peak due to the intact ion $[Me_3Pd(pz_3CH)]^+$ (*m/z* 365), but there is also a much weaker peak at *m/z* 335 due to $[MePd(pz_3CH)]^+$ formed by loss of Me_2. As the B1 voltage is raised the intensity of the peak at *m/z* 335 increases relative to that of the intact ion, confirming that the daughter ion arises from collisional activated decomposition. At B1 = 80 V the

TABLE 1. Electrospray mass spectrometric data for palladium(IV) compounds

Compound	Ions in ESMS (*m/z*) (low B1 voltage)	Daughter ions in CADMS or ESMS with high B1 voltage (*m/z*)
$[Me_2(C_3H_5)Pd(mim_2pyCH)]I$	$[Me_2(C_3H_5)Pd(mim_2pyCH)]^+$ (430)	$[Pd(mim_2pyCH)]^+$ (359)
	$[(C_3H_5)Pd(mim_2pyCH)]^+$ (400)	$[mim_2pyCH_2]^+$ (254)
	$[MePd(mim_2pyCH)]^+$ (374)	$[mim_2pyC]^+$ (252)
$[Me_3Pd(mim_2pyCH)]I$	$[Me_3Pd(mim_2pyCH)]^+$ (404)	$[Pd(mim_2pyCH)]^+$ (359)
	$[MePd(mim_2pyCH)]^+$ (374)	$[mim_2pyC]^+$ (252)
$[Me_2EtPd(mim_2pyCH)]I$	$[Me_2EtPd(mim_2pyCH)]^+$ (418)	$[Pd(mim_2pyCH)]^+$ (359)
	$[EtPd(mim_2pyCH)]^+$ (388)	$[mim_2pyCH_2]^+$ (254)
	$[MePd(mim_2pyCH)]^+$ (374)	$[mim_2pyC]^+$ (252)
$[Me_3Pd(pz_3CH)]BF_4$	$[Me_3Pd(pz_3CH)]^+$ (365)	$[MePd(pz_3CH)]^+$ (335)
	$[MePd(pz_3CH)]^+$ (335)	$[Pd(pz_3CH)]^+$ (320)
		$[Pd(pz_2C)]^+$ (252)
		$[Pd(pzC_2N_2)]^+$ (225)

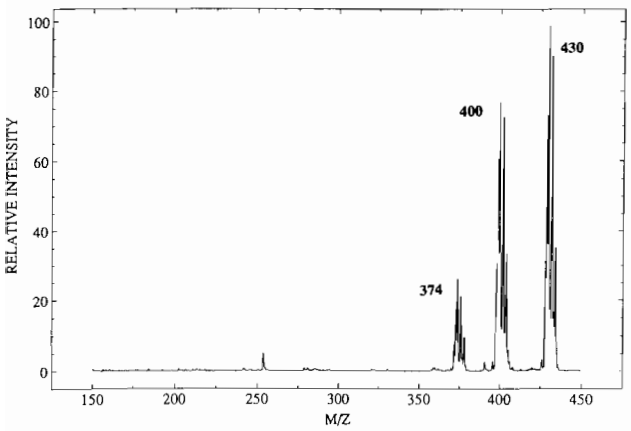


Fig. 1. Positive ion mass spectrum of $[Me_2(C_3H_5)Pd\{mim_2py)CH\}]I$ in methanol (B1 = 25 V).

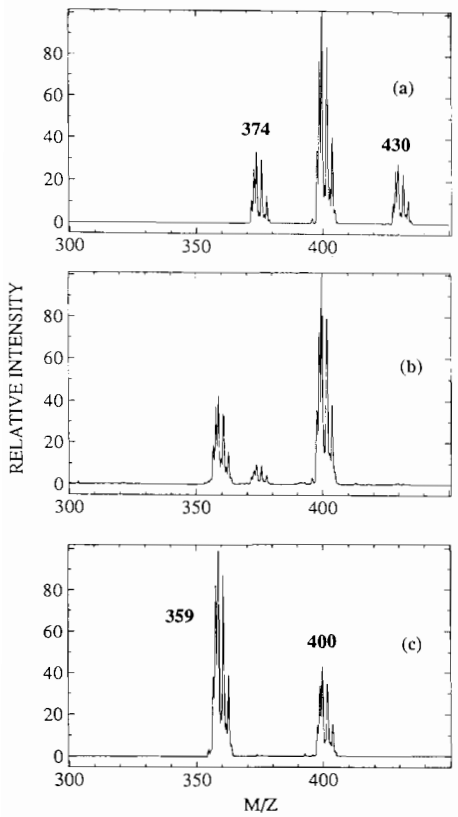


Fig. 2. Positive ion mass spectrum of $[Me_2(C_3H_5)Pd\{mim_2py)CH\}]I$ in methanol as a function of B1 voltage: (a) 40, (b) 80, (c) 100 V.

peaks at *m/z* 365 and 335 are both very weak and the base peak at *m/z* 320 corresponds to loss of all three methyl groups from the parent ion to give $[Pd(pz_3CH)]^+$. A peak at *m/z* 252 corresponds to further loss of the (pz + H) fragment to give $[Pd(pz_2C)]^+$ and this decomposition pathway will emerge as a commonly observed fragmentation pattern for many of the complexes containing similar pyrazole ligands. At B1 = 100 V a new peak at *m/z* 225 corresponds to loss of a further C_2H_3 fragment. The importance of examining the isotopic mass distribution to confirm the identification of peaks is nicely illustrated by comparison of the peaks at *m/z* 252 for this compound (which shows the palladium isotope pattern) and that derived from $[Me_2(C_3H_5)Pd(mim_2pyCH)]I$, discussed above, which does not contain palladium.

An alternative method of studying collision activation is via tandem mass spectrometry. Ions of particular *m/z* value (rather than the entire isotopic mass range) are passed through a collision cell into a second mass analyser. In the absence of any gas in the collision cell the gas phase stability of the ions can be assessed. Ions of *m/z* 365 from the mass distribution of $[Me_3Pd(pz_3CH)]^+$ at low ion source energy show a small amount of decomposition to $[MePd(pz_3CH)]^+$ on the timescale of this experiment (~100 μs), confirming the unstable nature of this ion. When argon is present in the collision cell, and using an accelerating voltage of 200 V in the collision cell, the same daughter ions are observed as in the ES mass spectrum with B1 = 100 V, although the intensity of the peak at *m/z* 225 is very low.

Platinum(IV) complexes

The marked differences between the stabilities of palladium(IV) and platinum(IV) are exemplified by the ES mass spectral behaviour of $[Me_3Pt(pz_3CH)]BF_4$ compared with that of its palladium analogue described above. At ion source energies up to 70 V the only significant peak is that due to the intact ion $[Me_3Pt(pz_3CH)]^+$ (*m/z* 454). Even at B1 = 100 V, where there is some fragmentation leading to daughter ions, there is no evidence of simple loss of Me_2 to give $[MePt(pz_3CH)]^+$. The daughter ions formed under these conditions are $[Pt(pz_3C)]^+$ (*m/z* 408), $[MePt(pz_2C)]^+$ (*m/z* 355) and $[Pt(pz_2C)]^+$ (*m/z* 340) with the latter two species being formed by elimination of (pz + H) from the tris(pyrazole) ligand as described above. The similar compound $[Ph_2MePt(pz_3CH)]I$ gives its intact ion (*m/z* 578) as the only species in its ES mass spectrum at low ion source energies, but at B1 = 80 V there is considerable fragmentation as shown in Table 2, which also contains data for all the platinum(IV) cations. The closely related complex $[Ph_2Pt(pz_3CH)I]I$ also gives only its intact ion (*m/z* 690) at low ion source energies with a number of daughter ions being produced both at higher B1 voltages and in the CADMS.

The compound $[Me_3Pt(pz_3CMe)]I$ gives only the intact ion (*m/z* 468) at ion source energies 25–70 V but at B1 = 100 V some fragmentation does occur. A relatively strong peak at *m/z* 422, corresponding to loss of 46 mass units from the intact ion, is unidentified.

TABLE 2. Electrospray mass spectrometric data for platinum(IV) compounds

Compound	Ions in ESMS (*m/z*) (low B1 voltage)	Daughter ions in CADMS or ESMS with high B1 voltage (*m/z*)
$[Me_3Pt(pz_3CH)]I$	$[Me_3Pt(pz_3CH)]^+$ (454)	$[Pt(pz_3C)]^+$ (408) $[MePt(pz_2C)]^+$ (355) $[Pt(pz_2C)]^+$ (340)
$[Ph_2MePt(pz_3CH)]I$	$[Ph_2MePt(pz_3CH)]^+$ (578)	$[PhMePt(pz_3C)]^+$ (500) $[Ph_2Pt(pz_2C)]^+$ (495) $[PhPt(pz_3CH)]^+$ (486) $[PhMePt(pz_2C)]^+$ (432) $[PhPt(pz_2C)]^+$ (418) $[Pt(pz_3C)]^+$ (408) $[MePt(pz_2C)]^+$ (355) $[Pt(pz_2C)]^+$ (341)
$[Ph_2Pt(pz_3CH)I]I$	$[Ph_2Pt(pz_3CH)I]^+$ (690)	$[PhPt(pz_3C)I]^+$ (612) $[Pt(pz_3CH)I]^+$ (536) $[PhPt(pz_3CH)]^+$ (486) $[Pt(pz_2C)I]^+$ (468) $[PhPt(pz_2C)]^+$ (418) $[Pt(pz_3C)]^+$ (408) $[Pt(pz_2C)]^+$ (341)
$[Me_3Pt(pz_3CMe)]I$	$[Me_3Pt(pz_3CMe)]^+$ (468)	422? $[MePt(pz_2C)]^+$ (356) $[Pt(pz_2C)]^+$ (341)
$[Ph_2MePt(pz_2mimCH)]I$	$[Ph_2MePt(pz_2mimCH)]^+$ (592)	$[PhPt(pz_2mimCH)]^+$ (500) $[PhPt(pzmimC)]^+$ (432)
$[Me_2Pt(pz_2mimCH)I]I$	$[Me_2Pt(pz_2mimCH)I]^+$ (580)	$[Pt(pz_2mimCH)I]^+$ (550) $[Pt(pzmimC)I]^+$ (482) $[Pt(pz_2mimCH)]^+$ (423) $[Pt(pzmimC)]^+$ (355) $[Pt(pz_2C)]^+$ (340)
$[Me_2Pt\{pz_2(L)CH\}py]I$ $(L=C_3H_2N_2)$	$[Me_2Pt\{pz_2(L)CH\}py]$ (517)	$[Me_2Pt\{pz_2(L)CH\}]^+$ (438) $[Pt\{pz(L)C]^+$ (340)
$[MeEtPt\{pz_2(L)CH\}py]I$ $(L=C_3H_2N_2)$	$[MeEtPt\{pz_2(L)CH\}py]$ (531)	$[MeEtPt\{pz_2(L)CH\}]^+$ (452) $[Pt\{pz_2(L)CH\}]^+$ (408) $[Pt\{pz(L)C]^+$ (340)
$[MeBzPt\{pz_2(L)CH\}py]I$ $(L=C_3H_2N_2)$	$[MeBzPt\{pz_2(L)CH\}py]$ (593)	$[MeBzPt\{pz_2(L)CH\}]^+$ (514) $[MeBzPt\{pz(L)C\}]^+$ (446) $[Pt\{pz(L)C\}]^+$ (340)
$[MePt\{pz_2(L)CH\}(CH_2CH_2pz)]Br$ $(L=C_3H_2N_2)$	$[MePt\{pz_2(L)CH\}(CH_2CH_2pz)]^+$ (518)	$[MePt\{pz(L)C\}(CH_2CH_2pz)]^+$ (450) $[HPt\{pz(L)C\}(CH_2CH_2pz)]^+$ (436) $[MePt\{pz(L)C\}(CH=CH_2)]^+$ (382) $[MePt\{pz(L)C\}]^+$ (355) $[Pt\{pz(L)C]^+$ (340)
$[Me_2Pt(CH_2CMepz_2)(py)]Cl$	$[Me_2Pt(CH_2CMepz_2)(py)]^+$ (479) $[Me_2Pt(CH_2CMepz_2)]^+$ (400)	

$Ph_2MePt(pz_2mimCH)]I$ gives the intact ion $[Ph_2MePt(pz_2mimCH)]^+$ (*m/z* 592) as the only significant peak in its ES mass spectrum at low ion source energies. At higher ion source energies the most abundant ions are $[PhPt(pz_2mimCH)]^+$ (*m/z* 500) and $[PhPt(pzmimC)]^+$ (*m/z* 432). The complex $[Me_2Pt(pz_2mimCH)I]I$ also gives only a single peak due to its intact ion (*m/z* 580) at low ion source energies, but at higher energies a number of daughter ions are produced as detailed in Table 2.

The cyclometallated complex $[Me_2Pt\{pz_2(C_3H_2N_2)CH\}py]I$ gives a very simple ES mass spectrum. At low ion source energies the peak due to the intact ion $[Me_2Pt\{pz_2(C_3H_2N_2)CH\}py]^+$ (*m/z* 517) is the only peak in the mass spectrum, but at B1 voltages of 50 V and above, a strong peak appears due to $[Me_2Pt\{pz_2(C_3H_2N_2)CH\}]^+$ (*m/z* 438) due to loss of the pyridine ligand. The CADMS shows an additional weak peak assigned to $[Pt\{pz(C_3H_2N_2)C\}]^+$ formed by loss of the usual (pz+H) fragment. The related compounds $[MeEtPt\{pz_2(C_3H_2N_2)CH\}py]I$ and $[MeBzPt\{pz_2(C_3H_2N_2)CH\}py]I$ give similar ES mass spectra with the intact ion peaks dominating the spectra at low ion source energies, although the fragmentation patterns

observed at higher B1 voltages are more complicated. Another complex containing a cyclometallated tris(pyrazole) ligand is $[MePt\{pz_2(C_3H_2N_2)CH\}(CH_2CH_2pz)]Br$. At low ion source energies, the only significant peak is that due to the intact ion $[MePt\{pz_2(C_3H_2N_2)CH\}(CH_2CH_2pz)]^+$ (*m/z* 518). At B1 = 60 V two new weaker peaks are observed at *m/z* 450, which corresponds to loss of the usual (pz + H), and *m/z* 436 which most likely corresponds to loss of Me from the *m/z* 450 ion by collisional activation, followed by protonation by acetic acid in the gas phase. At still higher ion source energies further fragmentation occurs as shown in Table 2.

In contrast, the pyridine adduct $[Me_2Pt(CH_2CMepz_2)(py)]Cl$ (Scheme 1) loses its pyridine ligand very readily so that at a B1 voltage of only 30 V the base peak is that due to $[Me_2Pt(CH_2CMepz_2)]^+$ (*m/z* 400) and that of the intact ion is relatively weak. Presumably the lability of the pyridine ligand in this complex compared with the previous examples is related to the *trans* influence of the alkyl carbon atom compared with aryl (pyrazole) carbon atoms in the other compounds. At higher ion source energies, loss of Me_2 and (pz + H) occurs.

Palladium(II) complexes

Data for all palladium(II) compounds are given in Table 3.

The compound $[Pd(py_3CH)_2](NO_3)_2$ gives only one peak in its ES mass spectrum at low ion source energies corresponding to the intact ion $[Pd(py_3CH)_2]^{2+}$ (*m/z* 300). The isotope pattern confirms the dipositive charge. As the B1 voltage is increased, the only daughter ions to appear in the spectrum are at *m/z* 246 and 248, assigned to $[py_3C]^+$ and $[py_3CH_2]^+$, respectively. The fragment $[py_3C]^+$ is analogous to the $[mim_2pyC]^+$ daughter ions seen in the spectra of Pd(IV) complexes, and $[py_3CH_2]^+$ is simply free ligand protonated by the acetic acid in the mobile phase in the spectrometer. At a low ion source energy of 30 V, the ES mass spectrum of $[Pd(pz_3CH)_2](BF_4)_2$ also shows the intact ion $[Pd(pz_3CH)_2]^{2+}$ (*m/z* 267) as the only significant peak. However, in contrast to the previous example only daughter ions containing palladium are observed at higher ion source energies. At B1 = 40 V a peak appears at *m/z* 233 due to loss of (pz + H) from one ligand to give $[Pd(pz_3CH)(pz_2C)]^{2+}$. At B1 = 60 V the dominant peak is due to $[Pd(pz_2C)_2]^{2+}$ (*m/z* 199) with the previously mentioned peaks now very weak.

The allyl complex $[(C_3H_5)Pd(pz_3CH)][(C_3H_5)PdBr_2]$ provides an example which can be usefully studied in both positive and negative ion modes. Even at ion source energies as high as 50 V, the only peak observed in the positive ion mode is due to the intact ion $[(C_3H_5)Pd(pz_3CH)]^+$ (*m/z* 361), but loss of (pz + H) to give $[(C_3H_5)Pd(pz_2C)]^+$ (*m/z* 293) occurs at B1 = 70 V. At B1 = 100 V, the base peak is at *m/z* 252, due to $[Pd(pz_2C)]^+$, and there are weaker peaks present at *m/z* 293 and 225, the latter being due to $[Pd(pzC_2N_2)]^+$. The pattern of breakdown of the intact ion therefore follows that established by the previous examples, but the resistance to loss of the allyl ligand is noteworthy and clearly emphasises the well known propensity of palladium to form stable compounds with this type of ligand. At B1 = 50 V the negative ion ES mass spectrum of $[(C_3H_5)Pd(pz_3CH)][(C_3H_5)PdBr_2]$ shows only two

TABLE 3. Electrospray mass spectrometric data for palladium(II) compounds

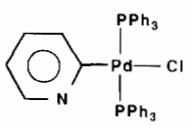
Compound	Ions in ESMS (*m/z*) (low B1 voltage)	Daughter ions in CADMS or ESMS with high B1 voltage (*m/z*)
$[Pd(py_3CH)_2](NO_3)_2$	$[Pd(py_3CH)_2]^{2+}$ (300)	$[py_3C]^+$ (246) $[py_3CH_2]^+$ (248)
$[Pd(pz_3CH)_2](BF_4)_2$	$[Pd(pz_3CH)_2]^{2+}$ (267)	$[Pd(pz_3CH)(pz_2C)]^{2+}$ (233) $[Pd(pz_2C)_2]^{2+}$ (199)
$[(C_3H_5)Pd(pz_3CH)][(C_3H_5)PdBr_2]$ (Cations)	$[(C_3H_5)Pd(pz_3CH)]^+$ (361)	$[(C_3H_5)Pd(pz_2C)]^+$ (293) $[Pd(pz_2C)]^+$ (252) $[Pd(pzC_2N_2)]^+$ (225)
(Anions)	$[(C_3H_5)PdBr_2]^-$ (307) $[PdBr_2]^-$ (266)	
$[(C_3H_5)Pd(phen)]Br$	$[(C_3H_5)Pd(phen)]^+$ (327)	
$[(C_3H_5)Pd(bipy)][(C_3H_5)PdBr_2]$ (Cations)	$[(C_3H_5)Pd(bipy)]^+$ (303)	$[Pd(bipy)]^+$ (262)
$[MePd(bipy)(\gamma\text{-pic})]BF_4$	$[MePd(bipy)(\gamma\text{-pic})]^+$ (370) $[MePd(bipy)]^+$ (277)	$[Pd(bipy)]^+$ (262)
$[Pd\{(C_6H_3)(CHMepy)_2\}(H_2O)]BF_4$	$[Pd\{(C_6H_3)(CHMepy)_2\}]^+$ (393)	$[\{(C_6H_3)(CHMepy)_2\}+H]^+$ (287)
[MePd(terpy)]I	$[MePd(terpy)]^+$ (354)	$[Pd(terpy)]^+$ (339) $[Pd(terpy\text{-}H)]^+$ (338)

peaks, one due to the intact ion $[(C_3H_5)PdBr_2]^-$ (*m/z* 307) and the other weaker peak at *m/z* 266 assigned to $[PdBr_2]^-$. The similar cationic species $[(C_3H_5)Pd(phen)]Br$ and $[(C_3H_5)Pd(bipy)][(C_3H_5)PdBr_2]$ also both give their intact ions in the positive ion mode, and for the latter cation the species $[Pd(bipy)]^+$ (*m/z* 261) was observed by tandem mass spectrometry.

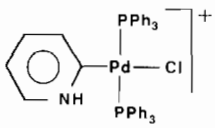
The positive ion ES mass spectrum of $[MePd(bipy)(\gamma\text{-pic})]BF_4$ at low ion source energy (B1 = 30 V) shows the intact ion $[MePd(bipy)(\gamma\text{-pic})]^+$ (370) as the base peak with a small peak at *m/z* 277 resulting from loss of the γ-pic ligand. At B1 = 70 V the peak due to the intact ion had almost disappeared and the base peak was at *m/z* 262, assigned to $[Pd(bipy)]^+$, although there was still a peak at *m/z* 277.

The complex $[Pd\{(C_6H_3)(CHMcpy)_2\}(H_2O)]BF_4$ (Scheme 1) was the only compound which failed to show its intact ion in the ES mass spectrum. At low ion source energies the only peak was that due to $[Pd\{(C_6H_3)(CHMepy)_2\}]^+$ (*m/z* 393) and at B1 = 100 V a peak appeared at *m/z* 287 which is due to the protonated ligand, although *m/z* 393 was still the base peak. Thus this complex very readily loses its water ligand, but thereafter is very stable in the gas phase.

An important aspect of ESMS is the very gentle nature of the transfer of ions from solution to the gas phase, and indeed only one compound failed to show its intact ion. Recently, a comparative study was made [20] of three ionisation methods for mass spectrometry using some palladium(II) and platinum(II) complexes of the types $MCl(R_N)(PPh_3)_2$ (R_N = 2-pyridyl, 2-pyrazyl, 2-pyrimidyl), which are not dissimilar to some of the compounds studied here. The methods investigated were electron impact (EI), fast atom bombardment (FAB) and laser induced vaporisation (LIV). Since the uncoordinated nitrogen atom of the ligand is known to be basic [21, 22], and hence likely to be protonated by the mobile phase to give a cation, it seemed to us appropriate to investigate one of these compounds to allow a comparison to be made between ESMS and the other ionisation techniques. The compound chosen for investigation was $Pd(Cl)(2\text{-py})(PPh_3)_2$ (Structure 1). Initial attempts to observe the protonated cation *m/z* 744 (Structure 2) by dissolving the solid in methanol, and relying on the mobile phase to protonate the complex, were unsuccessful, but addition of triphenylphosphine to the solution resulted in the ES mass



Structure 1.



Structure 2.

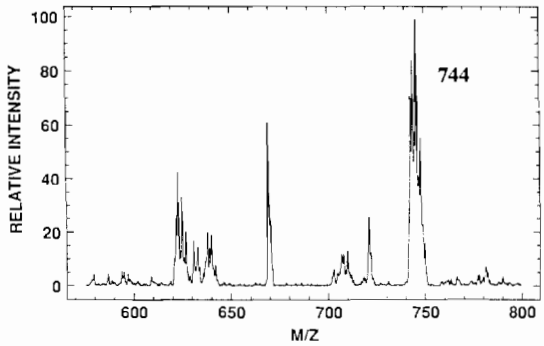
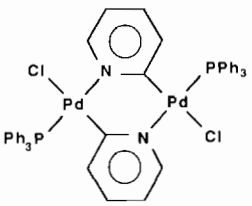


Fig. 3. Positive ion mass spectrum of $PdCl(2\text{-py})(PPh_3)_2$ in methanol to which has been added some PPh_3 (B1 = 30 V).



Structure 3.

spectrum shown in Fig. 3 (B1 = 30 V). Although a number of peaks are observed, that due to the intact ion $[Pd(Cl)(2\text{-pyH})(PPh_3)_2]^+$ is the base peak and provides unequivocal evidence for its existence in solution. As the B1 voltage is increased, so do the relative intensities of the peaks between 623 and 638. It was necessary to add triphenylphosphine since the compound dimerises [21] to form the neutral species shown in Structure 3, which cannot be protonated by the mobile phase in the spectrometer, but triphenylphosphine cleaves the dimer to regenerate $Pd(Cl)(2\text{-pyH})(PPh_3)_2$.

Although this spectrum does show more fragmentation than is usual in ESMS, it is far superior to the spectrum obtained by FAB-MS for which 166 peaks are tabulated [20] with the base peak due to PPh_3O and the peak due to $[Pd(Cl)(2\text{-pyH})(PPh_3)_2]^+$ had a relative intensity of only 1.8%. In addition, complex reactions with the thioglycerol matrix used in the FAB-MS experiment gave rise to many peaks of higher *m/z* value than 744, so identification of the molecular ion would be difficult without additional information. Our conclusion is that ESMS is superior to FAB-MS for this type of complex, provided the compound is ionic or can be readily converted to an ionic derivative.

Conclusions

It is apparent from this work that ESMS is a powerful technique for the characterisation of organometallic complexes of palladium and platinum in solution. In general, the relative ease of loss of the different ligands

by collisional activation with solvent molecules is consistent with the known chemistry of the systems, and thus provides a new method of investigating relative ordering of ligand bond strengths in these complexes, which can be applied in future to other systems.

Experimental

The compounds with polydentate ligands were prepared as described previously [11–18], as was PdCl(2-py)$(PPh_3)_2$ [21].

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Tech, Altrincham, Cheshire, UK) with a water/methanol/acetic acid (50:50:1%) mobile phase. The compounds were dissolved in either methanol or pyridine (2 mM) and this solution was then diluted 1:10 with methanol. 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 vaporisation nozzle of the electrospray ion source at a flow rate of $3\mu l\ min^{-1}$. Voltages at the first skimming electrode (B1) were varied between 100 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 25–30 V. Increasing the B1 voltage enhances the formation of daughter ions by collisions with solvent molecules within the ion source. In addition, ions of a particular *m/z* value (e.g. the peak maximum in an isotopic mass distribution) can be selected and passed through a collision cell into a second mass analyser. In the absence of gas in the collision cell the stabilities of the selected ions can be investigated. Collision activated decomposition (CAD) mass spectra of the selected ions were obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

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