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Electrospray Mass Spectrometric Study of Ionic Derivatives of Platinum(II) Dithiolates with Polyphosphines

Ray Colton,*[1] Vanda Tedesco,[2] and John C. Traeger[1]

Department of Chemistry, La Trobe University,
Bundoora 3083, Australia, and Inorganic Chemistry Section,
School of Chemistry, University of Melbourne,
Parkville 3052, Australia

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Introduction

Electrospray mass spectrometry (ESMS) is a recently developed technique which has been widely used in the structural analysis of large biomolecules.[3,4] The compound to be examined is dissolved in a suitable solvent, together with a small amount of organic acid to assist protonation, and then passed directly into the electrospray ion source of the mass spectrometer. This ionization technique is very soft and causes minimal fragmentation. In contrast, mass spectrometry of inorganic and organometallic compounds has usually involved volatilization of the sample and then ion formation in the gas phase by some technique such as electron impact, although assorted desorption techniques have also been used.[5] As a result, most studies with inorganic and organometallic compounds have been done on nonionic compounds, since ionic species are in general relatively involatile.

ESMS allows mass spectra to be generated from ionic species in solution and our approach has been to use ESMS for the first time to investigate a range of inorganic and organometallic compounds which are already ionic and for which the protonation step is unnecessary.[6] In this communication we describe the electrospray mass spectra of a number of ionic derivatives of platinum(II) dithiolates with polyphosphines of the general formula $[(\text{phosphine})\text{Pt}(\text{S-S})]\text{BPh}_4$ (S-S = dithiolate).[7-10] Some neutral derivatives of the type (polyphosphine)$\text{Pt}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})$ containing a pendant phosphine group, which cannot be directly observed by ESMS since they are uncharged, were converted to phosphonium compounds $[(\text{polyphosphineMe})\text{Pt}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})]\text{I}$ by reaction with MeI, and the ES mass spectra of these derivatives are reported also.

Results

About 2 μL of a 0.2 mM solution of the compounds in either dichloromethane or a dichloromethane/methanol (1:10) mixture was passed directly into the ion source of the electrospray mass spectrometer.[11] Figure 1a shows the ES mass spectrum for $[(\text{dpm})\text{Pt}(\text{dtp})]^+$ (dpm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; dtp = $\text{S}_2\text{P}(\text{OEt})_2$) while Figure 1b shows the comparison between the observed and calculated isotopic mass distribution. Table I lists the compounds examined, and in every case the molecular ion was observed with the correct isotopic mass distribution. With few exceptions the peak due to the molecular ion was the only one in the mass spectru, although occasionally weaker peaks at lower mass were observed. These are believed to be artifacts due to interaction of the dichloromethane solution of our compounds with the aqueous/methanol mobile phase which is continuously passed through the electrospray ion source of the instrument (see Experimental Section). The ES mass spectrum of $\{(\eta^2\text{-P}_3)\text{Pt}(\text{dtc})\}^+$ (P_3 = $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$; dtc = S_2CNEt_2) showed the molecular ion (*m/z* 967) and two others at *m/z* 983 and 999. These are believed to be due to oxidation to phosphine oxide of the pendant phosphine (*m/z* 983) and two phosphorus atoms (*m/z* 999) in the complex by interaction with the methanol solution referred to above. We have seen similar reactions with the monophosphonium salts of several polyphosphines when examined by ESMS.[12] The compounds $[(\eta^2\text{-P}_3)\text{Pt}(\text{dtc})]\text{BPh}_4$ and $[(\eta^2\text{-P}_3)\text{Pt}(\text{dtp})]\text{BPh}_4$ were reacted with MeI which converted the pendant phosphine to the phosphonium salt to generate the $[(\eta^2\text{-P}_3\text{Me})\text{Pt}(\text{dtc})]^{2+}$ and $[(\eta^2\text{-P}_3\text{Me})\text{Pt}(\text{dtp})]^{2+}$ cations, which were detected in the ES mass spectrum of the solution. Similarly, the neutral species $(\eta^2\text{-P}_3)\text{Pt}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})$, which cannot be detected by ESMS, was converted to $[(\eta^2\text{-P}_3\text{Me})\text{Pt}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})]^+$ and its ES mass spectrum was recorded.

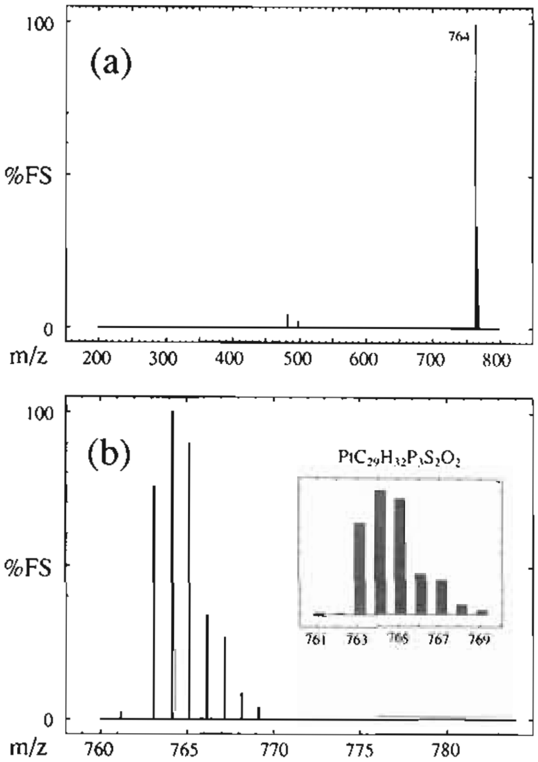

Figure 1. (a) ES mass spectrum of $[(\text{dpm})\text{Pt}(\text{dtp})]^+$ (b) Comparison of observed and calculated isotopic mass distribution for the $[(\text{dpm})\text{Pt}(\text{dtp})]^+$ molecular ion.

The ES mass spectrometer used here has the facility 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 analyzer.

The most intense molecular ion of each sample was passed into the second quadrupole mass filter in the absence of collision gas and in every case only the parent peak was observed. This shows that the ions are stable in the gas phase with no metastable decomposition on the time scale of this experiment, which is of the order of 100 μs.

We have previously shown[13] that dithiocarbamate (S_2CNEt_2), dithiocarbonate (S_2CO) and the dealkylated dithiophosphate ($\text{S}_2\text{P}\{\text{O}\}\text{OEt}$) are much stronger ligands to platinum(II) than dithiophosphate ($\text{S}_2\text{P}(\text{OEt})_2$) and xanthate ($\text{S}_2\text{CO}^n\text{Pr}$). In the presence of argon, collisional activated mass spectra of the mass selected parent ions at 200 V clearly reflect these differences.

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(2) University of Melbourne.
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Table I. Electrospray Mass Spectra

compound[a]	parent ion (m/z)[b]	fragments (m/z)[c]
$[(dpm)Pt(dtc)]BPh_4$	$[(dpm)Pt(dtc)]^+$ (727)	
$[(dpm)Pt(dtp)]BPh_4$	$[(dpm)Pt(dtp)]^+$ (764)	
$[(\eta^3\text{-}P_2P')Pt(dtc)]BPh_4$	$[(P_2P')Pt(dtc)]^+$ (877)	$[(PhP'CH_2CH_2PPh_2)Pt(dtc)]^+$ (664) $[(PhP'CH_2CH_2PPh_2)PtS]^+$ (548)
$[(\eta^3\text{-}P_2P')Pt(dtp)]BPh_4$	$[(P_2P')Pt(dtp)]^+$ (914)	$[(P_2P')PtS]^+$ (761) $[Pt\text{-}P\text{-}CH_2]^+$ (241)
$[(\eta^3\text{-}P_2P')Pt(xan)]BPh_4$	$[(P_2P')Pt(xan)]^+$ (864)	$[(P_2P')PtS]^+$ (761) $[(P_2P')Pt]^+$ (729)
$[(\eta^2\text{-}P_3)Pt(dtc)]BPh_4$	$[(P_3)Pt(dtc)]^+$ (967)	$[\{CH_2{=}C(CH_2PPh_2)_2\}Pt(dtc)]^+$ (767) $[\{CH_2{=}C(CH_2PPh_2)CH_2PPh\}Pt(dtc)]^+$ (691)
	$[(P_3O)Pt(dtc)]^+$ (983) $[(P_3O_2)Pt(dtc)]^+$ (999)	
$[(\eta^2\text{-}P_3Me)Pt(dtc)]IBPh_4$	$[(P_3Me)Pt(dtc)]^{2+}$ (491)	
$[(\eta^2\text{-}P_3)Pt(dtp)]BPh_4$	$[(P_3)Pt(dtp)]^+$ (1004)	$[(P_3)Pt]^+$ (819)
$[(\eta^2\text{-}P_3Me)Pt(dtp)]IBPh_4$	$[(P_3Me)Pt(dtp)]^{2+}$ (509.5)	
$[(\eta^2\text{-}P_3Me)Pt(S_2P\{O\}OEt)]I$	$[(\eta^2\text{-}P_3Me)Pt(S_2P\{O\}OEt)]^+$ (990)	
$[(\eta^4\text{-}P_3P')Pt(xan)]BPh_4$	$[(P_3P')Pt(xan)]^+$ (1000)	$[(P_3P')PtS]^+$ (897) $[(P_3P')Pt]^+$ (865) $[\{P'(CH_2CH_2PPh_2)_2\}Pt]^+$ (653)

[a] dpm = $Ph_2PCH_2PPh_2$, P_2P' = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$, P_3 = $CH_3C(CH_2PPh_2)_3$, P_3P' = $P(CH_2CH_2PPh_2)_3$, dtc = S_2CNEt_2, dtp = $S_2P(OEt)_2$, and xan = S_2CO^nPr. [b] Mass based upon ^{195}Pt. [c] Collision-activated fragmentation, 200 V, argon.

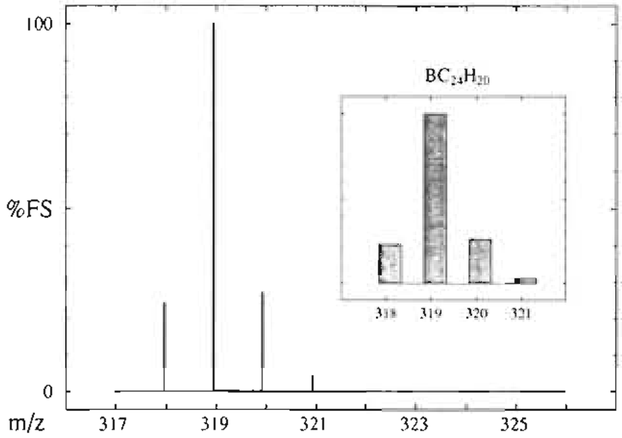

Figure 2. Comparison of observed and calculated isotopic mass distribution in the ES mass spectrum for the $[BPh_4]^-$ molecular ion.

The fragmentation mass spectra derived from the mass selected parent ions of $[(P_2P')Pt(dtp)]^+$ and $[(P_2P')Pt(xan)]^+$ (P_2P' = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$) show ions containing intact P_2P' and loss of all or part of the dithiolate. In contrast, the same type of mass spectrum for $[(P_2P')Pt(dtc)]^+$ shows fragmentation of both the P_2P' ligand and the dtc ligand. It appears therefore, that the ordering of ligand strengths determined for the dithiolates in solution may also be applicable in the gas phase. The compounds $[(\eta^2\text{-}P_3)Pt(dtc)]^+$ and $[(\eta^2\text{-}P_3)Pt(dtp)]^+$ show similar behavior although in this case the intensities of the peaks in the MS/MS were very low.

Since all the platinum compounds were examined as their tetraphenylborate salts, it seemed appropriate to examine the negative ion ES mass spectrum of $[BPh_4]^-$. Figure 2 shows the observed mass spectrum together with the calculated spectrum.

Discussion

Although ESMS is now well established in biological applications, there have been no detailed studies of inorganic and organometallic systems. The results reported in this paper demonstrate the application of electrospray mass spectrometry to the study of species in an area of chemistry quite different from that in which the technique was first developed. We believe that ESMS will have a profound effect in the study of inorganic and organometallic systems since it allows for the first time the observation of mass spectra from ionic species in solution.

The identities of all these complexes in solution have been previously established by multinuclear magnetic resonance methods, and the aim of this paper is to demonstrate that ESMS gives reliable indications of the species present in solution. In each case ESMS gave parent ions in the gas phase of the same composition as that deduced in the solution phase by NMR spectroscopy. That is, in each case the ion was transferred from the solution phase to the gaseous phase without any chemical change, emphasising the "soft" nature of this step. It is obvious that multi-NMR spectroscopy and ESMS are a very powerful combination of techniques for the study of species in solution.

The observation of different collisionally activated fragmentation patterns depending upon the nature of the dithiolate opens up new possibilities for the study of the comparative bonding capabilities of ligands in many inorganic and organometallic systems. The collisional activation mass spectra obtained by ESMS are not as rich as those obtained by electron impact, but on the basis of the results reported in this paper, they show promise of being particularly informative in mixed ligand situations.

The results reported in this paper demonstrate that, in principle, charged (+*ve* or −*ve*) phosphine complexes of any metal can be examined by ESMS providing they are soluble and stable in an appropriate solvent. All compounds examined in this work are nonlabile on the NMR time scale and are regarded as static in terms of molecular dynamics. We propose to extend our exploration of ESMS to systems which are labile on the NMR time scale at room temperature.

Experimental Section

The compounds were prepared as their tetraphenylborate salts as described earlier.[7-10] They were dissolved in dichloromethane solution (2 mM), and this solution was then diluted 1:10 with either dichloromethane or methanol. The diluted solution was injected directly via a Rheodyne model 7125 injector with a 10-μL loop using a Carlo Erba Phoenix micro 20 LC syringe pump to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 2 μL min^{-1}. Since the mobile phase was an aqueous/methanol solution of acetic acid, the sample solution was preceded and followed by aqueous methanol through the loop and into the nozzle. It is at the solution interfaces that side reactions can occur under the conditions of vaporization at the nozzle. In some cases reported in this paper these reactions result in oxidation of pendant phosphine groups, but without disruption of the rest of the molecule, giving a mass spectrum containing the expected parent ion and another weaker one at 16 m/z units higher due to the oxide.

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