Inorganica Chimica Acta, 220 (1994) 99–105

π-Bonded alkene and arene complexes of silver(I): an electrospray mass spectrometric study

Allan J. Canty
Chemistry Department, University of Tasmania, Hobart 7001 (Australia)

Ray Colton*
Chemistry Department, La Trobe University, Bundoora 3083 (Australia)

(Received December 15, 1993)

Abstract

Electrospray mass spectra have been observed for a number of alkene and arene complexes of Ag(I) formed by the interaction of $AgNO_3$ and the organometallic ligand in water/methanol solution. The ES mass spectra show that almost all the alkene and arene ligands in stoichiometric excess form labile 1:2 cationic complexes with Ag(I) which are easily decomposed by collisional activation to the 1:1 species. However, with a deficiency of organic ligand polymeric species are observed. The cation $[Ag(cod)_2]^+$ (cod = 1,5-cyclooctadiene) was reacted with a variety of other potential ligands, such as PPh_3, $AsPh_3$, $PhSCH_2SPh$ etc. In most cases, mixed complexes $[Ag(cod)(ligand)]^+$ were observed, and excess ligand usually produced $[Ag(ligand)_2]^+$.

Key words: Electrospray mass spectrometry; Silver complexes; Alkene complexes; Arene complexes

Introduction

π-Bonded alkene and arene complexes of Ag(I) have a long and venerable history which has been well surveyed in an excellent review [1]. These complexes are simply prepared in solution by mixing a silver salt with the hydrocarbon in a water/methanol mixture. The constitution of the alkene complexes in solution has usually been determined by indirect means such as those based on solubility studies of the hydrocarbon in solutions of silver salts [2–5] and measurements of the distribution of the hydrocarbon between aqueous solutions of silver salts and carbon tetrachloride [6–9]. Gas chromatography using silver nitrate/ethylene glycol columns provides more precise data on equilibrium formation constants of the complexes [10–13]. Proton NMR spectra of many 1:2 silver alkene complexes have been studied [14], but those of silver arene compounds have been generally unhelpful since many of the complexes are labile in solution [15].

Silver(I) alkene and arene complexes are rather unstable and many of them decompose upon attempted isolation. However, examples of 1:1 and 1:2 adducts, as well as other stoichiometries [1], have been characterised in the solid state and a number of structures have been determined by X-ray crystallography [1, 16–19]. Many of the structures are polymeric and none contain discrete silver alkene cations since in all cases the anions are coordinated to the metal atom. In addition, the stoichiometries of the solids isolated for a particular alkene or arene depend markedly upon the nature of the associated anion, all of which suggests that the structures of the isolated solids may give little insight into the nature of the species actually present in the aqueous methanol solutions.

Electrospray mass spectrometry (ESMS) provides a new method of investigating labile species in solution. The technique was first used to investigate mass spectra of very large bio-molecules [20–22], but we have shown that it is also applicable to a wide variety of inorganic and organometallic systems. In particular, it has been used to investigate alkyl derivatives of several metals [23–25] and also labile exchanging systems such as Cu(I) phosphine and phenanthroline complexes [26], Hg(II) phosphine complexes [27] and cationic metal dithiocarbamate complexes [28, 29].

In this paper we use ESMS to investigate the nature of complexes in solution formed by Ag(I) with a range of alkene and arene molecules.

---

*Author to whom correspondence should be addressed.

0020-1693/94/$07.00
SSDI 0020-1693(94)03861-H

Experimental

Complexes between Ag(I) and the organic ligands were prepared in solution by mixing an aqueous solution of $AgNO_3$ (approx. 2 mM) and an equal volume of methanol containing a few drops of the ligand. If a precipitate formed, sufficient methanol was added to give a clear solution, and this was then diluted 1:10 with methanol and the diluted solution was injected directly into the ES mass spectrometer. Ag(I) alkene/phosphine complexes were prepared by addition of a few drops of a methanol or dichloromethane solution of the phosphine to the Ag(I)–alkene mixture before the final dilution.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (VG Bio Tech, Altrincham, Ches., UK) using a water/methanol/acetic acid (50:50:1%) mobile phase. The diluted solutions of the compounds, prepared as described above, were injected directly into the spectrometer via a Rheodyne injector equipped with a 10 μl loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporisation nozzle of the electrospray ion source at a flow rate of 3 μl min^{-1}. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approximately 3 l min^{-1} and 100 ml min^{-1}, respectively. Pressure in the mass analyser region was usually about 3×10^{-5} torr. The compounds in this study give strong signals in their ES mass spectra and typically 8–12 signal averaged spectra were required to give a good signal to noise ratio. Increasing the voltage on the first skimmer electrode (B1) may induce fragmentation caused by collisions with solvent molecules in the region of the nozzle where the pressure is close to atmospheric. Measurements were made at a B1 voltage of 40 V unless stated otherwise.

Results and discussion

All peaks in the electrospray mass spectra are identified by the most abundant peak in the isotopic mass distribution. In all cases the agreement between experimental and calculated isotopic mass distribution was excellent. Silver has only two isotopes (^{107}Ag, ^{109}Ag) of almost equal abundances so that complexes containing one, two or three silver atoms are readily distinguishable by simple inspection of the mass spectrum since the isotopic mass distribution appears as a doublet, a triplet and a quartet, respectively (neglecting the relatively small effects of ^{13}C and ^{34}S). Furthermore, if the cation is singly charged the separation between the peaks is two mass units and for doubly charged cations it is only one mass unit.

Silver(I) alkene and arene complexes

Figure 1(a) shows the ES mass spectrum (B1 = 35 V) for a water/methanol solution of a mixture of 1,5-cyclooctadiene and $AgNO_3$ (< 2:1 molar proportions). The mass spectrum is dominated by the peak at *m/z* 323 which is due to the intact ion $[Ag(C_8H_{12})_2]^+$, but there is also a relatively weak peak at *m/z* 494 which is assigned to $[Ag_2(C_8H_{12})_2(NO_3)]^+$. Figure 1(b) shows the ES mass spectrum with B1 = 45 V and the new peak at *m/z* 215 is due to the ion $[Ag(C_8H_{12})]^+$ which is formed from $[Ag(C_8H_{12})_2]^+$ by collisional activation within the ion source, where the pressure is close to atmospheric. Figure 1(c) shows the ES mass spectrum at a B1 voltage of 60 V and the collisionally activated decomposition of $[Ag(C_8H_{12})_2]^+$ is now almost complete. These are low skimmer voltages to cause such extensive

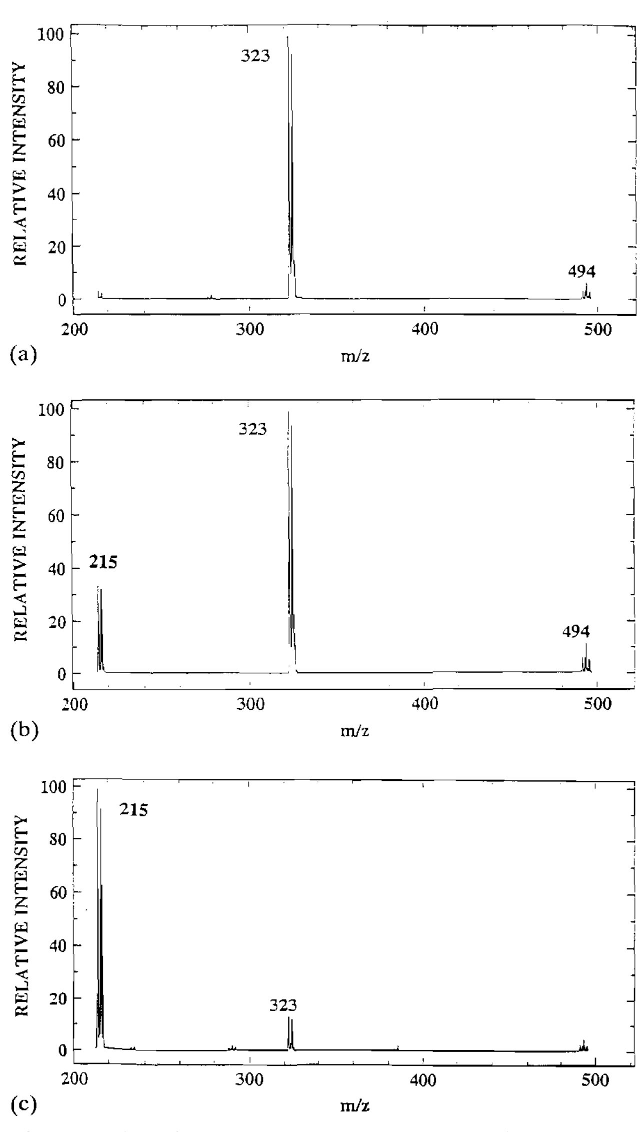


Fig. 1. Positive ion ES mass spectra for a solution containing 1,5-cyclooctadiene and silver nitrate (< 2:1) at different collision energies: (a) B1 = 35 V, (b) B1 = 45 V, (c) B1 = 60 V.

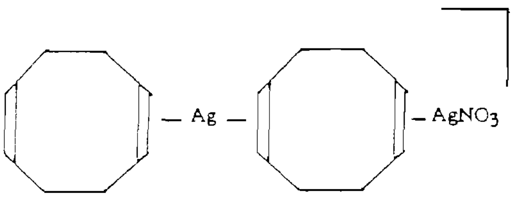
decomposition, which suggests that the bis(alkene) complex is very labile. When more C_8H_{12} is added to give a molar ratio of diene:silver > 2:1, then only the peak due to $[Ag(C_8H_{12})_2]^+$ is observed at low B1 voltages. Presumably the structure of the cation containing two silver atoms is as shown in Scheme 1 and it is probably derived from a neutral species containing two nitrate groups. It is important to note that ESMS only detects the ionic species in a solution and in rapidly exchanging systems such as these silver alkenes, which may well involve equilibria between ionic and neutral components, it can give no indication of the position of these equilibria.

When silver nitrate was added to norbornadiene only species containing one silver atom were observed, and at low B1 voltages the ES mass spectrum is dominated by peaks at *m*/*z* 291 and 307 with a weaker peak at *m*/*z* 323 which are assigned to $[Ag(C_7H_8)_2]^+$, $[Ag(C_7H_8)(C_7H_8O)]^+$ and $[Ag(C_7H_8O)_2]^+$, respectively. At slightly higher B1 voltages $[Ag(C_7H_8)]^+$ (*m*/*z* 199) and $[Ag(C_7H_8O)]^+$ (*m*/*z* 215) become dominant showing that these complexes are also easily fragmented. The ES mass spectrum of a solution containing the isomeric cycloheptatriene and silver nitrate is dominated by the peak due to $[Ag(C_7H_8)_2]^+$ (*m*/*z* 291) with only a very weak peak due to $[Ag(C_7H_8)(C_7H_8O)]^+$. However, even at B1 = 35 V, there is a significant peak due to $[Ag(C_7H_8)]^+$ (*m*/*z* 199) and a weak peak at *m*/*z* 462 assigned to $[Ag_2(C_7H_8)_2(NO_3)]^+$.

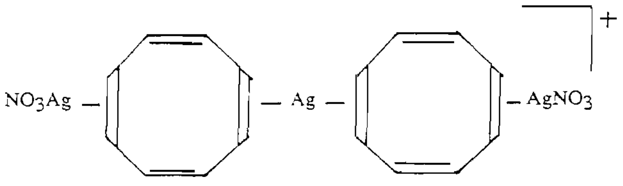
Another triene, *cis*,*cis*,*trans*-cyclododecatriene, $C_{12}H_{18}$, after reaction with silver nitrate gives ES mass spectra which are generally similar to those given by cycloheptatriene, except that peaks containing the oxidised alkene are somewhat more intense. All data are summarised in Table 1.

A solution of 1,3,5,7-cyclooctatetraene, C_8H_8, and silver nitrate (less than 2:1 molar proportions) gives an ES mass spectrum in which the base peak is at *m*/*z* 315, assigned to $[Ag(C_8H_8)_2]^+$, but there are a number of other peaks with significant intensities which have no analogues in the systems previously discussed. A peak at *m*/*z* 419, which contains only one silver atom, can only be assigned to $[Ag(C_8H_8)_3]^+$ and two overlapping triplet peaks at *m*/*z* 483 and 486 are due to $[Ag_2(C_8H_8)_2(OAc)]^+$ and $[Ag_2(C_8H_8)_2(NO_3)]^+$, respectively, with the acetate being derived from the mobile phase used in the spectrometer. Another peak at *m*/*z* 655, which the isotope pattern shows to contain three silver atoms, is assigned to $[Ag_3(C_8H_8)_2(NO_3)_2]^+$. In the presence of an excess of the alkene, only $[Ag(C_8H_8)_2]^+$ is observed at low B1 voltages whilst $[Ag(C_8H_8)]^+$ is readily generated in the gas phase at higher B1 voltages. Presumably these additional species observed with C_8H_8, but not with the other alkenes, are possible because C_8H_8 is better able to act as a bridging group between silver atoms as shown in Scheme 2. This is the only alkene to show an ion corresponding to a tris(alkene) cation and the likely structure is shown in Scheme 3.

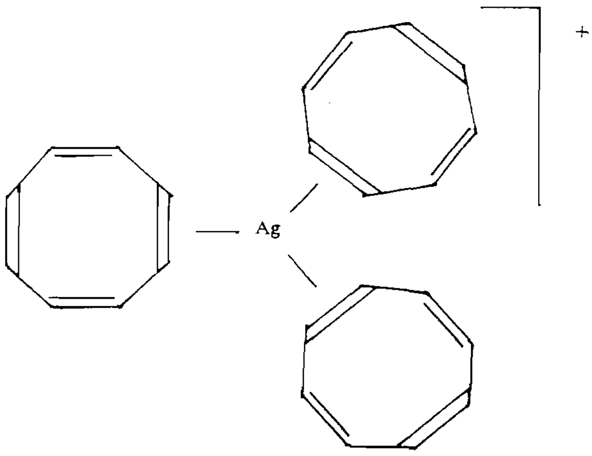
Water/methanol solutions of a number of arenes with silver nitrate were also examined and their ES mass spectra are very similar to those of the alkene complexes. For example, when the arene is mesitylene and at a B1 voltage of 40 V, the ES mass spectrum is dominated by a peak at *m*/*z* 347 which is due to the intact ion $[Ag(C_9H_{12})_2]^+$. However there are much weaker peaks at higher *m*/*z* values which are assigned to $[Ag_2(C_9H_{12})(OAc)]^+$ (395), $[Ag_2(C_9H_{12})(NO_3)]^+$ (398) and $[Ag_2(C_9H_{12})_2(NO_3)]^+$ (518). At slightly higher collisional energies, a peak at *m*/*z* 227 due to $[Ag(C_9H_{12})]^+$ becomes dominant. In the presence of excess mesitylene, only $[Ag(C_9H_{12})_2]^+$ is observed at low B1 voltages. Other arenes give similar ES mass spectra except for the case of benzene itself, for which only $[Ag(C_6H_6)]^+$ is observed. All data for silver arene complexes are summarised in Table 1.



Scheme 1.



Scheme 2.



Scheme 3.

TABLE 1. Electrospray mass spectral data for complexes of silver nitrate with alkenes and arenes

Alkene or arene	Ions (*m/z*)
1,5-Cyclooctadiene	$[Ag(C_8H_{12})]^+$ (215); $[Ag(C_8H_{12})_2]^+$ (323); $[Ag_2(C_8H_{12})_2(NO_3)]^+$ (494)
Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)	$[Ag(C_7H_8)]^+$ (199); $[Ag(C_7H_8O)]^+$ (215); $[Ag(C_7H_8)_2]^+$ (291); $[Ag(C_7H_8)(C_7H_8O)]^+$ (307); $[Ag(C_7H_8O)_2]^+$ (323)
Cycloheptatriene	$[Ag(C_7H_8)]^+$ (199); $[Ag(C_7H_8)_2]^+$ (291); $[Ag_2(C_7H_8)_2(NO_3)]^+$ (462)
c,c,t-1,5,9-Cyclododecatriene	$[Ag(C_{12}H_{18})]^+$ (269); $[Ag(C_{12}H_{18})_2]^+$ (431); $[Ag(C_{12}H_{18})(C_{12}H_{18}O)]^+$ (447); $[Ag(C_{12}H_{18}O)_2]^+$ (463); $[Ag_2(C_{12}H_{18})_2(NO_3)]^+$ (602)
1,3,5,7-Cyclooctatetraene	$[Ag(C_8H_8)]^+$ (211); $[Ag(C_8H_8)_2]^+$ (315); $[Ag(C_8H_8)_3]^+$ (419); $[Ag_2(C_8H_8)_2(OAc)]^+$ (483); $[Ag_2(C_8H_8)_2(NO_3)]^+$ (486); $[Ag_2(C_8H_8)_3(NO_3)]^+$ (590); $[Ag_3(C_8H_8)_2(NO_3)_2]^+$ (655)
Benzene	$[Ag(C_6H_6)]^+$ (185)
Toluene	$[Ag(C_7H_8)_2]^+$ (291); $[Ag_2(C_7H_8)(OAc)]^+$ (367); $[Ag_2(C_7H_8)(NO_3)]^+$ (370); $[Ag_2(C_7H_8)_2(NO_3)]^+$ (462)
o-Xylene	$[Ag(C_8H_{10})]^+$ (213); $[Ag(C_8H_{10})_2]^+$ (319)
Mesitylene	$[Ag(C_9H_{12})]^+$ (227); $[Ag(C_9H_{12})_2]^+$ (347); $[Ag_2(C_9H_{12})(OAc)]^+$ (395); $[Ag_2(C_9H_{12})(NO_3)]^+$ (398); $[Ag_2(C_9H_{12})_2(NO_3)]^+$ (518)

The impression given by an examination of the solid state data on isolated complexes is that there is a wide range of stoichiometries for silver(I) complexes with different organometallic ligands. The ESMS data show that this variety also exists in solution, but only when the molar proportions of alkene/arene to silver nitrate is less than 2:1. Once this limit is reached most of the ligands behave in a uniform manner to give only the 2:1 complex in solution, the only exceptions being benzene for which only $[Ag(C_6H_6)]^+$ was detected and C_8H_8 which gives the tris(alkene) complex. However, all the evidence suggests that the complexes are labile in solution, so the nature of the solid isolated from the solutions will be dependent upon the relative solubilities of the complexes and extra factors associated with the solid state such as packing effects and lattice energies.

The implied lability suggests that the alkenes may be readily displaced by other ligands so reactions in solution of $[Ag(C_8H_{12})_2]^+$, $[Ag(1,5\text{-cod})_2]^+$, with a variety of reagents have been investigated.

Exchange reactions of $[Ag(1,5\text{-cod})_2]^+$

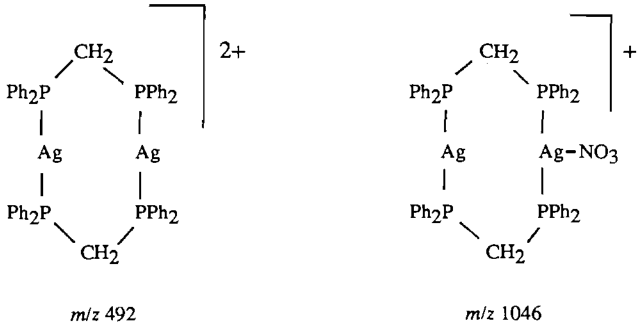
Addition of a small quantity of PPh_3 to $[Ag(cod)_2]^+$ gave an ES mass spectrum (B1 = 35 V) with three strong peaks at *m/z* 477, 323 and 215 due to $[Ag(cod)(PPh_3)]^+$, $[Ag(cod)_2]^+$ and $[Ag(cod)]^+$, respectively. At a B1 voltage of 50 V, the strongest peaks are at *m/z* 369 and 215 although those at *m/z* 477 and 323 are still present. The new peak at *m/z* 369 is assigned to $[Ag(PPh_3)]^+$ which is a collisionally activated product ion which could have only originated from $[Ag(cod)(PPh_3)]^+$ as this solution did not show a peak at *m/z* 631 due to $[Ag(PPh_3)_2]^+$. Since only a small amount of PPh_3 was added to the solution, this spectrum shows that PPh_3 easily displaces 1,5-cod from silver(I), and furthermore the collisionally activated mass spectrum confirms that a considerable amount of $[Ag(cod)(PPh_3)]^+$ decomposes by loss of diene rather than phosphine. Under the conditions of this experiment we are unable to say that all the cation decomposes by this route since the product ion formed by loss of PPh_3 would be $[Ag(cod)]^+$, and although this ion is observed, it is also produced from $[Ag(cod)_2]^+$ by collisional activation. Confirmation of the superior ligand strength of PPh_3 over 1,5-cod was demonstrated by addition of further PPh_3 to the original mixture. The subsequent ES mass spectrum showed a very strong peak at *m/z* 631 due to $[Ag(PPh_3)_2]^+$, a weak one at *m/z* 477 due to $[Ag(cod)(PPh_3)]^+$ and no peaks due to other ions containing 1,5-cod. All data are summarised in Table 2. Essentially similar ES mass spectral results were obtained from the reaction of $[Ag(cod)_2]^+$ with tricyclohexylphosphine, PCy_3, except that additional peaks were observed due to the formation of some phosphine oxide in the electrospray process. This has been observed before [26] for some phopshine complexes, especially those of PCy_3. Reaction of $[Ag(cod)_2]^+$ with $AsPh_3$ also gives analogous ES mass spectra (Table 2).

When $[Ag(cod)_2]NO_3$ is reacted with diphosphines rather different types of product are observed and in most cases mixed phosphine/alkene complexes are not observed. When a small amount of dpm (dpm = $Ph_2PCH_2PPh_2$) is added to a solution of $[Ag(cod)_2]^+$ the ES mass spectrum shows the presence of $[Ag(cod)_2]^+$ itself and peaks at *m/z* 662 and 491 due to $[Ag_2(dpm)(NO_3)]^+$ and $[Ag(dpm)]^+$, respectively. No peak corresponding to the ion $[Ag(cod)(dpm)]^+$ is observed, but there is a peak of moderate intensity at *m/z* 615 which can be assigned to $[Ag(cod)(dpmO)]^+$ (dpmO = $Ph_2P(O)CH_2PPh_2$). There is also a weak peak at *m/z* 507 assigned to $[Ag(dpmO)]^+$. Since there is still a silver/alkene complex present in the solution, the data suggests that for some reason $[Ag(cod)(dpm)]^+$ is inherently unstable. Varying the B1 voltage dem-

TABLE 2. ES mass spectral data for derivatives of the silver(I) 1,5-cyclooctadiene complex

Mixture	Ions (*m/z*)
$[Ag(cod)_2]^+ + PPh_3$	$[Ag(cod)]^+$ (215); $[Ag(cod)_2]^+$ (323); $[Ag(PPh_3)]^+$ (369); $[Ag(cod)(PPh_3)]^+$ (477); $[Ag(PPh_3)_2]^+$ (631)
$[Ag(cod)_2]^+ + PCy_3$	$[Ag(PCy_3)]^+$ (387); $[Ag(OPCy_3)]^+$ (403); $[Ag(cod)(PCy_3)]^+$ (495); $[Ag(cod)(OPCy_3)]^+$ (511); $[Ag(PCy_3)_2]^+$ (667); $[Ag(PCy_3)(OPCy_3)]^+$ (683)
$[Ag(cod)_2]^+ + AsPh_3$	$[Ag(cod)]^+$ (215); $[Ag(cod)_2]^+$ (323); $[Ag(AsPh_3)]^+$ (413); $[Ag(cod)(AsPh_3)]^+$ (521); $[Ag(AsPh_3)_2]^+$ (719)
$[Ag(cod)_2]^+ + dpm$	$[Ag(cod)_2]^+$ (323); $[Ag(dpm)]^+$ (491); $[Ag_2(dpm)_2]^{2+}$ (492); $[Ag(dpmO)]^+$ (507); $[Ag(cod)(dpmO)]^+$ (615); $[Ag_2(dpm)(NO_2)]^+$ (662); $[Ag_2(dpm)_2(NO_3)]^+$ (1046)
$[Ag(cod)_2]^+ + dpe$	$[Ag(cod)_2]^+$ (323); $[Ag(dpe)]^+$ (505); $[Ag_2(dpe)(NO_3)]^+$ (676); $[Ag_3(dpe)_3(NO_3)]^{2+}$ (790.5); $[Ag(dpe)_2]^+$ (905); $[Ag_2(dpe)_2(NO_3)]^+$ (1074)
$[Ag(cod)_2]^+ + ape$	$[Ag(cod)_2]^+$ (323); $[Ag(ape)]^+$ (549); $[Ag(cod)(ape)]^+$ (657); $[Ag_2(ape)(NO_3)]^+$ (720); $[Ag_2(cod)(ape)(NO_3)]^+$ (828)
$[Ag(cod)_2]^+ + psm$	$[Ag(cod)]^+$ (215); $[Ag(cod)_2]^+$ (323); $[Ag(psm)]^+$ (341); $[Ag(cod)(psm)]^+$ (449); $[Ag_2(psm)(OAc)]^+$ (507); $[Ag(psm)_2]^+$ (573); $[Ag_2(psm)_2(NO_3)]^+$ (742)
$[Ag(cod)_2]^+ + pse$	$[Ag(cod)]^+$ (215); $[Ag(cod)_2]^+$ (323); $[Ag(pse)]^+$ (355); $[Ag(cod)(pse)]^+$ (463); $[Ag(pse)_2]^+$ (601); $[Ag_2(pse)_2(NO_3)]^+$ (770)

onstrated that the peak at *m/z* 491 is generated by collisionally activated decomposition of $[Ag_2(dpm)(NO_3)]^+$ and, importantly, the isotopic mass distribution for the peak at *m/z* 491 confirms the ion contains one silver atom and has only a single charge. When more dpm is added to the solution all the remaining alkene is displaced from silver and the ES mass spectrum is dominated by two peaks at *m/z* 492 and 1046. However, the peak at *m/z* 492 has a different isotopic pattern to the peak previously observed at *m/z* 491 and it shows the presence of two silver atoms in a doubly charged cation which is identified as $[Ag_2(dmp)_2]^{2+}$. The peak at *m/z* 1046 is due to the nitrate adduct of that ion, $[Ag_2(dpm)_2(NO_3)]^+$. It is common in ESMS [27] for doubly charged cations to form a monoanion adduct, so that these two ions essentially provide two ways of observing the same species. Both of these ions may be considered to be ionised derivatives of $Ag_2(dpm)_2(NO_3)_2$ which has been characterised by X-ray crystallography [30]. In the solid state there is a puckered Ag_2P_4 ring and the nitrate groups are each monodentate to one silver atom. It is therefore proposed that the ions $[Ag_2(dpm)_2]^{2+}$ and $[Ag_2(dpm)_2(NO_3)]^+$ have generally similar structures as shown in Scheme 4, but the conformation of the rings in the ionised forms is not known. There is also a weaker peak at *m/z* 909 which is not identified.



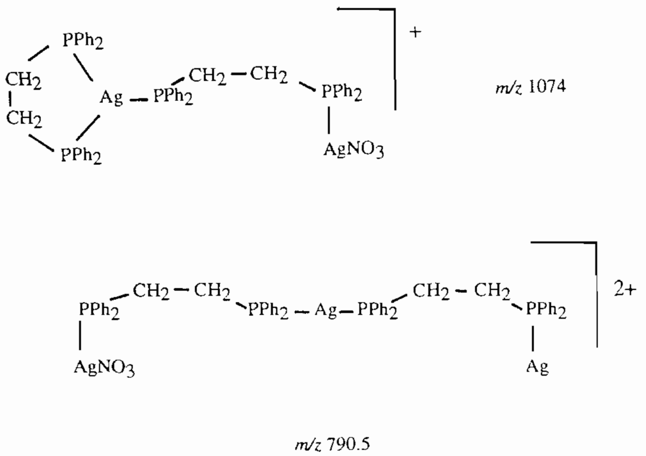
m/z 492 *m/z* 1046

Scheme 4.

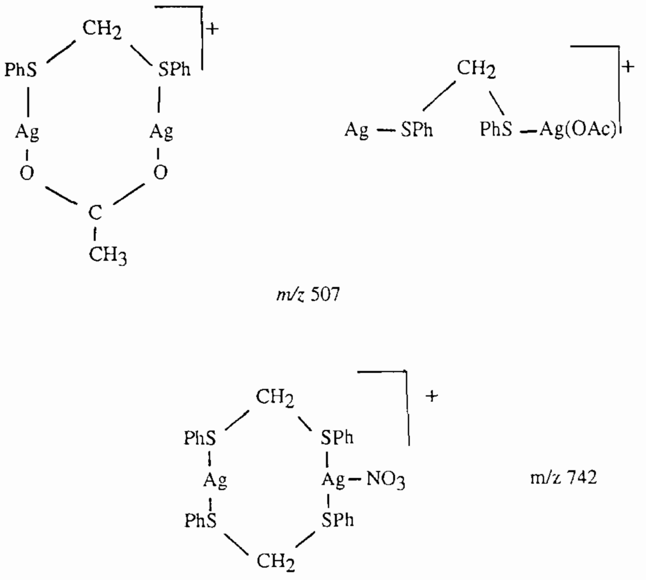
Slightly different products are observed in the reaction of $[Ag(cod)_2]NO_3$ with dpe (dpe = $Ph_2PCH_2CH_2PPh_2$), but these differences merely reflect the well known differences in the properties of the diphosphine ligands themselves. When small amounts of dpe are added to $[Ag(cod)_2]^+$, the ES mass spectrum shows peaks at *m/z* 505 and 676 assigned to $[Ag(dpe)]^+$ and $[Ag_2(dpe)(NO_3)]^+$, respectively, analogous to those observed with dpm. However, upon addition of more dpe further strong peaks appear at *m/z* 905 and 1074, assigned to $[Ag(dpe)_2]^+$ and $[Ag_2(dpe)_2(NO_3)]^+$, respectively, together with a weak peak at *m/z* 790.5. The isotopic mass distribution for this peak shows that it is due to a doubly charged cation containing three silver atoms which is identified as $[Ag_3(dpe)_3(NO_3)]^{2+}$. Dpe tends not to form the bridged complexes which are such a feature of dpm chemistry and instead it forms linear polymeric species. On this basis the structures in Scheme 5 are suggested for these silver dpe complexes observed by ESMS.

The main species observed by ESMS following interaction of $[Ag(cod)_2]^+$ and ape (ape = $Ph_2PCH_2CH_2AsPh_2$) are in general similar to those formed by dpe (Table 2) but, interestingly, weak peaks are observed which can be assigned to $[Ag(cod)(ape)]^+$ (*m/z* 657) and $[Ag_2(cod)(ape)(NO_3)]^+$ (*m/z* 828). The observation of these signals suggests that steric interaction of the phenyl groups of dpm and dpe with coordinated cod renders the mixed diphosphine/alkene complexes unstable, but with ape the larger arsenic atom decreases this interaction so that weak peaks due to the mixed ligand complexes are observed.

The potentially bidentate sulfur ligand $PhSCH_2SPh$ (psm) was reacted with $[Ag(cod)_2]^+$ and the ES mass



Scheme 5.



Scheme 6.

spectrum showed a number of ions were present in the solution including $[Ag(cod)_2]^+$, $[Ag(psm)]^+$ (*m/z* 341), $[Ag(cod)(psm)]^+$ (*m/z* 449), $[Ag_2(psm)(OAc)]^+$ (*m/z* 507), $[Ag(psm)_2]^+$ (*m/z* 573), $[Ag_2(psm)_2(NO_3)]^+$ (*m/z* 742). The fact that both $[Ag(cod)_2]^+$ and $[Ag(psm)_2]^+$ are present simultaneously indicates that the olefin and the sulfur donor ligand have comparable ligand strengths towards silver(I). The structure of $[Ag_2(psm)(OAc)]^+$ could be either linear or cyclic as shown in Scheme 6 and the most likely structure for $[Ag_2(psm)_2(NO_3)]^+$ is also shown in the Scheme, analogous to the dpm complexes described earlier. The isotopic mass distribution pattern for the peak at *m/z* 341 shows that it is due to $[Ag(psm)]^+$ and not $[Ag_2(psm)_2]^{2+}$. Reaction between $[Ag(cod)_2]^+$ and $PhSCH_2CH_2SPh$ (pse) led to the observation of similar ions and data are given in Table 2.

Conclusions

The most important conclusion to be drawn from this work is that it provides further evidence that ESMS is a technique most suitable for the study of labile complexes in solution. The silver alkene and arene complexes in solution have proved to be rather intractable to study by other techniques as a direct result of their lability. Solid state structures have revealed unsymmetrical coordination of arenes to silver and the observation by ESMS of ions which appear to have arene ligands bridging between two silver atoms strongly implies that this type of bonding is retained in solution.

The reactions of $[Ag(cod)_2]^+$ with various ligands confirm that the alkene is readily displaced and in general the nature of the products is as expected from prior knowledge of the chemistry of the added ligands.

Acknowledgement

We thank La Trobe University for a SCAEF major equipment grant which assisted in the purchase of the electrospray mass spectrometer.

References

1 C.D.M. Beverwijk, G.J.M. van den Kerk, A.J. Leusink and J.G. Noltes, *Organomet. Chem. Rev. A*, *5* (1970) 215.
2 G.K. Helmkamp, F.L. Carter and H.J. Lucas, *J. Am. Chem. Soc.*, *79* (1957) 1306.
3 R.M. Keefer, L.J. Andrews and R.E. Kepner, *J. Am. Chem. Soc.*, *71* (1949) 3644.
4 L.J. Andrews and R.W. Keefer, *J. Am. Chem. Soc.*, *72* (1950) 5733.
5 N. Ogimachi, L.J. Andrews and R.M. Keefer, *J. Am. Chem. Soc.*, *78* (1956) 2210.
6 H.J. Lucas, R.S. Moore and D. Pressman, *J. Am. Chem. Soc.*, *65* (1943) 230.
7 K.N. Trueblood and H.J. Lucas, *J. Am. Chem. Soc.*, *74* (1952) 1338.
8 J.G. Traynham and J.R. Olechowski, *J. Am. Chem. Soc.*, *81* (1959) 571.
9 T. Fueno, O. Kajimoto and J. Furukawa, *Bull. Chem. Soc. Jpn.*, *41* (1968) 782.
10 E. Gil-Av and J. Herling, *J. Phys. Chem.*, *66* (1962) 1208.
11 M.A. Muhs and F.T. Weiss, *J. Am. Chem. Soc.*, *84* (1962) 4697.
12 R.J. Cvetanovic, F.J. Duncan, W.E. Falconer and R.S. Irwin, *J. Am. Chem. Soc.*, *87* (1965) 1827.
13 H. Schnecko, *Anal. Chem.*, *40* (1968) 1391.
14 H.W. Quinn, J.S. McIntyre and D.J. Peterson, *Can. J. Chem.*, *43* (1965) 2896.
15 D.F.R. Gilson and C.A. McDowell, *J. Chem. Phys.*, *39* (1963) 1825.
16 G. Bressan, R. Broggi, M.P. Lachi and A.L. Segre, *J. Organomet. Chem.*, *9* (1967) 355.
17 I.W. Bassi and G. Fagherazzi, *J. Organomet. Chem.*, *13* (1968) 535.

18 D.J. Robinson and C.H.L. Kennard, *J. Chem. Soc., Chem. Commun.,* (1968) 914.

19 F.S. Mathews and W.N. Lipscomb, *J. Phys. Chem., 63* (1959) 845.

20 J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong and C.M. Whitehouse, *Science, 246* (1989) 64.

21 R.D. Smith, J.A. Loo, C.G. Edmonds, C.J. Barinaga and H.R. Udseth, *Anal. Chem., 62* (1990) 882.

22 R.D. Smith, J.A. Loo, R.R. Ogorzalek Loo, M. Busman and H.R. Udseth, *Mass Spectrom. Rev., 10* (1991) 359.

23 A.J. Canty, P.R. Traill, R. Colton and I.M. Thomas, *Inorg. Chim. Acta, 210* (1993) 91.

24 A.J. Canty, R. Colton and I.M. Thomas, *J. Organomet. Chem., 455* (1993) 283.

25 A.J. Canty and R. Colton, *Inorg. Chim. Acta, 215* (1994) 179.

26 R. Colton, B.D. James, I.D. Potter and J.C. Traeger, *Inorg. Chem., 32* (1993) 2626.

27 R. Colton and D. Dakternieks, *Inorg. Chim. Acta, 208* (1993) 173.

28 A.M. Bond, R. Colton, J.C. Traeger and J. Harvey, *Inorg. Chim. Acta, 212* (1993) 233.

29 A.M. Bond, R. Colton, A. D'Agostino and J.C. Traeger, *Inorg. Chem., 32* (1993) 3952.

30 D.M. Ho and R. Bau, *Inorg. Chem., 22* (1983) 4073.