Copper(I) Tetrahydroborate Derivatives Containing Phosphine and Phenanthroline Ligands: An Electrospray Mass Spectrometric Study of Species in Solution

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Electrospray mass spectra have been obtained from dichloromethane/methanol for cationic species existing in solutions of copper(I) tetrahydroborate derivatives containing phosphine- and phenanthroline-type ligands. Complexes of the type (L-L)Cu(PPh_3)(BH_4) (L-L = phenanthroline ligand) exist in solution as cationic $[(L\text{-}L)Cu(PPh_3)]^+$ species which are easily observed by electrospray mass spectrometry (ESMS). The triphenylphosphine ligand is labile and readily exchanges with excess triphenylphosphine, or another monodentate phosphine, at rates which are moderately fast on the ^{31}P NMR time scale at room temperature. However, under these conditions the $[(L\text{-}L)Cu(PPh_3)_2]^+$ cation can be observed by ESMS. When two different phosphines are present, two $[(L\text{-}L)Cu(PR_3)]^+$ ions and all three possible $[(L\text{-}L)Cu(PR_3)_2]^+$ cations are observed. Thus ESMS can observe individual cations from a solution in which the species are rapidly exchanging. Tandem MS/MS spectra show that the $[(L\text{-}L)Cu(PR_3)]^+$ cations readily lose phosphine and the $[(L\text{-}L)Cu(PR_3)_2]^+$ cations are very unstable in the gas phase toward loss of phosphine. Reaction of (L-L)Cu(PR_3)(BH_4) with 1 mol of L-L gives $[(L\text{-}L)_2Cu]^+$ ions which are observed in the ES mass spectrum. Interaction of $[(L\text{-}L)_2Cu]^+$ and a different phenanthroline complex $[(L'\text{-}L')_2Cu]^+$, or interaction of $[(L\text{-}L)_2Cu]^+$ with free L′-L′, gives all three possible bis(phenanthroline)copper cations, thus demonstrating that the phenanthroline ligands are also labile. The compound $(PPh_3)_2Cu(BH_4)$ exists in solution as cationic $[Cu(PPh_3)_2]^+$, which is also observable by ESMS. Addition of excess PPh_3 gives fast ligand exchange (NMR), but ESMS shows the presence of both $[Cu(PPh_3)_2]^+$ and $[Cu(PPh_3)_3]^+$ ions. Addition of 2 mol of another phosphine (PR_3) to $[Cu(PPh_3)_2]^+$ also gives sharp averaged ^{31}P NMR signals for each phosphine at room temperature, but the ES mass spectrum shows peaks corresponding to all the bis(phosphine) and tris(phosphine) cations. When 2 mol of each of two different phosphines are added to 1 mol of $[Cu(PPh_3)_2]^+$, the ES mass spectrum gives peaks for every possible combination of bis(phosphine)- and tris(phosphine)copper cations.

Introduction

The compounds (L-L)Cu(PPh_3)(BH_4) (L-L = phen = 1,10-phenanthroline or substituted phen) are known to involve coordinated tetrahydroborate ligands in the solid state,[1] but it is also known[2] that in solution ionic species are formed in the presence of excess phosphine (conductivity measurements) and the reaction in solution is thought to be

$$(L\text{-}L)Cu(PPh_3)(BH_4) + PPh_3 \rightleftharpoons [(L\text{-}L)Cu(PPh_3)_2][BH_4] \qquad (1)$$

However, it has also been noted[1a] that this reaction gives rise to a sharp exchange-averaged phosphorus-31 NMR signal whose position varies with the amount of phosphine added, so the solution behavior is complicated. In nonprotic solvents, in the presence of excess phosphine, the compounds (phen)Cu(PPh_3)(BH_4) and (3,4,7,8-tmp)Cu(PPh_3)(BH_4) (tmp = Me_4phen) react with CO_2 to give ionic derivatives $[(L\text{-}L)Cu(PPh_3)_2][HB(O_2CH)_3]$ or $[(L\text{-}L)Cu(PPh_3)_2][H_2B(O_2CH)_2]$. These cations may be isolated and characterized as their BF_4^- and BPh_4^- salts. In protic solvents the CO_2 reaction gives formato complexes.[2] When the compounds (L-L)Cu(PPh_3)(BH_4) are reacted with a second mole of L-L ligand, the cations $[Cu(L\text{-}L)_2]^+$ are formed. Crystal structures of several ions of this type have been determined, and all display tetrahedral geometry.[3–5] In the solid state, the complex $(PPh_3)_2Cu(BH_4)$ contains the tetrahydroborate ligand coordinated in a bidentate fashion,[6] and the structure of $(PPh_3)_2Cu(B_3H_8)$ is similar.[7]

Thus, there is ample evidence that ionic species may be present in solutions of (L-L)Cu(PPh_3)(BH_4) although their nature is not well established. The cationic $[Cu(L\text{-}L)_2]^+$ species are well established, and it is likely that $(PPh_3)_2Cu(BH_4)$ might also give ionic solutions. It seemed to us that the new technique of electrospray mass spectrometry (ESMS), which enables ions in solution to be investigated by mass spectrometry, might provide some useful insights into the solution chemistry of these interesting systems.

ESMS provides a method of transferring preexisting ions from solution to the gas phase. The technique is very soft and causes minimal fragmentation. ESMS is now well established in the characterization of large biomolecules such as proteins.[8,9] These are protonated in solution with an organic acid, and a family of peaks is observed due to different degrees of protonation of the protein. For example, horse heart myoglobin (MW 16 951) 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. Although the biochemical applications demonstrate that ESMS links solution- and gas-phase studies, the technique has not been applied in a systematic manner to inorganic and organometallic systems.

We have recently been investigating the use of ESMS on a wide range of charged inorganic and organometallic compounds.

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Anions and cations for which ES mass spectra have been obtained[10] include $[Fe(C_5H_5)_2]^+$, $[PF_6]^-$, and $[S_2Mo_{18}O_{62}]^{4-}$. 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; S-S = dithiolate ligand)[11] and of phosphonium cations derived from a number of polyphosphines.[12] A feature of these studies was that intact ions were always observed, emphasizing the "soft" nature of the process generating gas-phase ions. The term "intact ion" is used in situations where the original species (in this case in solution) and that observed in the gas phase are the same, whereas the term "molecular ion" is reserved for situations, as in most conventional MS techniques, where a neutral species is converted to an ion of the same molar mass in the gas phase.[13] However, in those circumstances the original species and the ionic species observed in the gas phase are not the same.

In our previous studies we have deliberately studied systems where a single, well-characterized species is present in solution in order to establish that ESMS does indeed give a good indication of the ionic species present in a solution. In this paper we describe electrospray mass spectra for copper(I) cations containing phenanthroline and/or phosphine ligands. This is the first time the technique has been applied to an inorganic system which is not yet fully understood, and it is also the first application of ESMS to inorganic compounds which are undergoing rapid ligand exchange.

Experimental Section

Compounds were prepared by the methods described by Cariati and Naldini.[14] Ligand abbreviations: phen = 1,10-phenanthroline, 4-mp = 4-methyl-1,10-phenanthroline (similarly for 5-mp); 2,9-dmp = 2,9-dimethyl-1,10-phenanthroline (similarly for 3,4-dmp, 4,7-dmp); 3,4,7,8-tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer[15] using a water/methanol/acetic acid mobile phase. The compounds were dissolved in dichloromethane (2 mM), and this solution was then diluted 1:10 with methanol. The diluted solution was directly injected into the spectrometer via a Rheodyne injector with a 10-μL loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 3 L min^{-1} and 100 mL min^{-1}, respectively. Voltages on the first skimmer electrode (B1) were varied between 70 V and the minimum possible consistent with retaining a stable ion jet. This varied from time to time but was usually in the range 25–35 V. Pressure in the mass analyzer region was usually about 3×10^{-5} Torr. The compounds in this study give very strong signals in the ES mass spectra, and typically four to eight signal-averaged spectra were required to give an acceptable signal to noise ratio.

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 analyzer. At low ion energies in the absence of introduced collision gas, the relative stabilities of these ions can be investigated. Collision-activated-decomposition (CAD) mass spectra of the selected precursor 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.

Phorphorous-31 NMR spectra were recorded on a Bruker AM-300 spectrometer.

Results

Throughout this paper m/z values are given for the most intense peak in the isotope mass distribution. In all cases, the experimental and calculated isotopic mass distributions agree well.

A. (L-L)Cu(PR$_3$)(BH$_4$) Complexes. Solutions of these complexes in dichloromethane/methanol (1:10) give strong peaks in the ES mass spectrum due to the cations $[(L\text{-}L)Cu(PR_3)]^+$. Figure 1a shows the ES mass spectrum for $(phen)Cu(PPh_3)(BH_4)$, which gives a peak due to the intact ion $[(phen)Cu(PPh_3)]^+$ (m/z 505). The mass spectrum is extremely clean, typical of the spectra reported in this paper, and the lack of fragmentation emphasizes the soft nature of the process for generating ions in the gas phase. With only residual gas in the collision cell, MS/MS of the mass selected cations $[(L\text{-}L)Cu(PR_3)]^+$ displayed some decomposition (loss of phosphine) in the second mass analyzer. In the presence of argon in the collision cell, and with an accelerating voltage of 200 V, all of these cations show loss of the phosphine ligand in their CAD mass spectra. Figure 1b shows a typical CAD mass spectrum, in this case for $[(phen)Cu(PPh_3)]^+$.

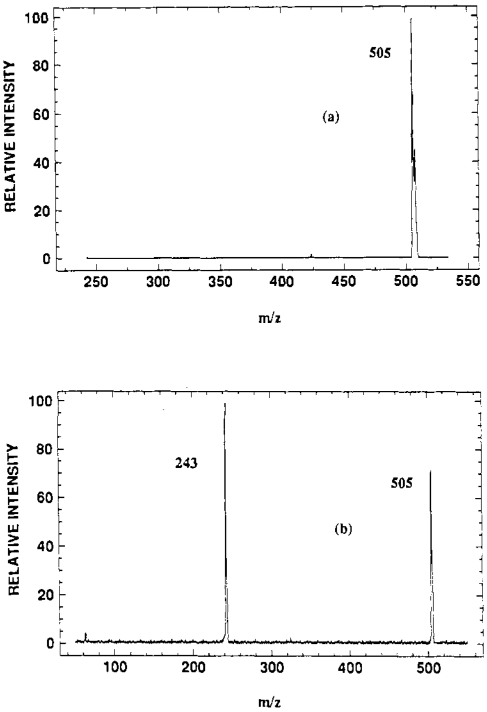

Figure 1. (a) Positive-ion ES mass spectrum of $(phen)Cu(PPh_3)(BH_4)$ (B1 = 40 V). (b) CAD mass spectrum of $[(phen)Cu(PPh_3)]^+$ (200 V, argon).

Phosphorus-31 NMR spectra of $(L\text{-}L)Cu(PR_3)(BH_4)$ complexes are broad at room temperature and undergo exchange with excess phosphine, so the loss of phosphine from the gaseous ions (which are the same species as those in solution) is consistent with the solution behavior. Since the NMR spectra are so broad, they are not suitable for use in the study of phosphine-exchange reactions at room temperature, but ESMS can be used. Addition of an approximately equimolar amount of tri-*m*-tolylphosphine (Pmt) to $[(5\text{-mp})Cu(PPh_3)]^+$ in dichloromethane/methanol causes two peaks to occur in the ES mass spectrum (B1 = 50 V) corresponding to the intact ions ($[5\text{-mp})Cu(PPh_3)]^+$ (m/z 519) and $[(5\text{-mp})Cu(Pmt)]^+$ (m/z 561). The identity of the peak at higher m/z was absolutely confirmed by its CAD mass spectrum, which showed loss of Pmt (m/z 304) to give $[(5\text{-mp})Cu]^+$ (m/z 257). In the absence of introduced gas in the collision cell, a small amount of decomposition was still observed. At a lower ion source energy (B1 = 32 V) the peaks at m/z 519 and 561 still dominate the mass spectrum but weak signals are also observed which are due to $[(5\text{-mp})Cu(PPh_3)_2]^+$ (m/z 781), $[(5\text{-mp})Cu(PPh_3)(Pmt)]^+$ (m/z 823), and $[(5\text{-mp})Cu(Pmt)_2]^+$ (m/z 865). These cations are unstable in the gas phase since MS/MS experiments reveal considerable decomposition ~40–60% with no deliberately added gas in the collision cell. Analogous results were obtained by reaction of $[(5\text{-mp})Cu(PPh_3)]^+$ with tris(*o*-methoxyphenyl)phosphine (Pom). Similar results were obtained by reacting $[(phen)Cu(PPh_3)]^+$ with Pmt and Pom. All data are given in Table I.

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Table I. Electrospray Mass Spectral Data for Copper Cations Containing Phenanthroline Ligands

compound	ions (ESMS) (m/z)[a]
(phen)Cu(PPh_3)(BH_4)	[(phen)Cu(PPh_3)]$^+$ (505)
(4-mp)Cu(PPh_3)(BH_4)	[(4-mp)Cu(PPh_3)]$^+$ (519)
(5-mp)Cu(PPh_3)(BH_4)	[(5-mp)Cu(PPh_3)]$^+$ (519)
(3,4-dmp)Cu(PPh_3)(BH_4)	[(3,4-dmp)Cu(PPh_3)]$^+$ (533)
(4,7-dmp)Cu(PPh_3)(BH_4)	[(4,7-dmp)Cu(PPh_3)]$^+$ (533)
(3,4,7,8-tmp)Cu(PPh_3)(BH_4)	[(3,4,7,8-tmp)Cu(PPh_3)]$^+$ (561)
(phen)Cu(PPh_3)(BH_4) + Pmt	[(phen)Cu(PPh_3)]$^+$ (505), [(phen)Cu(Pmt)]$^+$ (547), [(phen)Cu(PPh_3)$_2$]$^+$ (767), [(phen)Cu(PPh_3)(Pmt)]$^+$ (809), [(phen)Cu(Pmt)$_2$]$^+$ (851)
(phen)Cu(PPh_3)(BH_4) + Pom	[(phen)Cu(PPh_3)]$^+$ (505), [(phen)Cu(Pom)]$^+$ (595), [(phen)Cu(PPh_3)$_2$]$^+$ (767), [(phen)Cu(PPh_3)(Pom)]$^+$ (857), [(phen)Cu(Pom)$_2$]$^+$ (947)
(5-mp)Cu(PPh_3)(BH_4) + Pmt	[(5-mp)Cu(PPh_3)]$^+$ (519), [(5-mp)Cu(Pmt)]$^+$ (561), [(5-mp)Cu(PPh_3)$_2$]$^+$ (781), [(5-mp)Cu(PPh_3)(Pmt)]$^+$ (823), [(5-mp)Cu(Pmt)$_2$]$^+$ (865)
(5-mp)Cu(PPh_3)(BH_4) + Pom	[(5-mp)Cu(PPh_3)]$^+$ (519), [(5-mp)Cu(Pom)]$^+$ (609), [(5-mp)Cu(PPh_3)$_2$]$^+$ (781), [(5-mp)Cu(PPh_3)(Pom)]$^+$ (871), [(5-mp)Cu(Pom)$_2$]$^+$ (961)
(5-mp)Cu(PPh_3)(BH_4) + $AsPh_3$	[(5-mp)Cu(PPh_3)]$^+$ (519), [(5-mp)Cu($AsPh_3$)]$^+$ (563)
(5-mp)Cu(PPh_3)(BH_4) + 5-mp	[(5-mp)$_2$Cu]$^+$ (451)
(3,4-dmp)Cu(PPh_3)(BH_4) + 3,4-dmp	[(3,4-dmp)$_2$Cu]$^+$ (479)
[(2,9-dmp)$_2$Cu]$^+$ + [(5-mp)$_2$Cu]$^+$	[(5-mp)$_2$Cu]$^+$ (451), [(5-mp)(2,9-dmp)Cu]$^+$ (465), [(2,9-dmp)$_2$Cu]$^+$ (479)
[(2,9-dmp)$_2$Cu]$^+$ + 3,4,7,8-tmp	[(2,9-dmp)$_2$Cu]$^+$ (479), [(2,9-dmp)(3,4,7,8-tmp)Cu]$^+$ (507), [(3,4,7,8-tmp)$_2$Cu]$^+$ (535)

[a] Most intense peak of isotopic mass distribution.

Interestingly, addition of an approximately equimolar quantity of $AsPh_3$ to a solution of [(5-mp)Cu(PPh_3)]$^+$ caused almost no change in the mass spectrum, which showed a strong peak due to [(5-mp)Cu(PPh_3)]$^+$ itself (m/z 519) and a very weak peak due to [(5-mp)Cu($AsPh_3$)]$^+$ (m/z 563). Addition of an excess of $AsPh_3$ did produce a slightly stronger peak for [(5-mp)Cu($AsPh_3$)]$^+$, but there is no doubt that copper prefers to bond to phosphine rather than arsine on the basis of these observations. Thus ESMS can be used effectively to study competition reactions in solution for ligands such as arsines, which could never be studied by NMR methods because of the absence of a suitable NMR nucleus.

B. (L-L)$_2$Cu(BH_4) Complexes. Reaction of (L-L)Cu(PPh_3)(BH_4) compounds with 1 mol of L-L in dichloromethane/methanol gives (L-L)$_2$Cu(BH_4) species,[14] which in solution are ionized to give [(L-L)$_2$Cu]$^+$. ES mass spectra are easily observed for these cations. MS/MS spectra in the absence of argon collision gas show slight decomposition to give [(L-L)Cu]$^+$, thus suggesting some lability of the phenanthroline ligands. CAD mass spectra at 200 V show much more substantial loss of a phenanthroline ligand. Lability of the phenanthroline ligands was confirmed both by mixing two different [(L-L)$_2$Cu]$^+$ complexes and by reacting ([L-L)$_2$Cu]$^+$ with a different free phenanthroline in dichloromethane at room temperature. In each case, the ES mass spectrum showed the presence of all three possible bis(phenanthroline)copper cations. CAD mass spectra showed that, in the case of mixed cations, loss of the lighter phenanthroline was favored. Data are given in Table I.

C. (PR_3)$_2$Cu(BH_4) Complexes. In the solid state, these compounds contain coordinated tetrahydroborate ligands,[2] but their solutions in dichloromethane/methanol give strong ES mass spectra which show the presence of the intact ion [Cu(PR_3)$_2$]$^+$. The ES mass spectrum of a solution of (PPh_3)$_2$Cu(BH_4) shows a very strong peak at m/z 587 due to [Cu(PPh_3)$_2$]$^+$. In the absence of gas in the collision cell, the MS/MS spectrum of [Cu(PPh_3)$_2$]$^+$ gives only the precursor ion, showing it to be stable in the gas phase. However, the CAD mass spectrum of the ion m/z 587 (argon, 200 V) gives a product ion at m/z 325, which is [Cu(PPh_3)]$^+$. At room temperature, the phosphorus-31 NMR spectrum of (PPh_3)$_2$Cu(BH_4) in $CDCl_3$ is sharp and addition of triphenylphosphine gives a single sharp signal whose position varies with the amount of phosphine added, as has been noted earlier.[1a] This demonstrates that fast phosphine exchange is occurring and the peak observed is the exchange-averaged signal. It is likely that the exchange occurs via rapid formation and dissociation of the tris(phosphine)copper complex, as has been shown for similar phosphine complexes of other metals.[16] After addition of excess triphenylphosphine to (PPh_3)$_2$Cu(BH_4), the ES mass spectrum shows peaks due to both [Cu(PPh_3)$_2$]$^+$ and [Cu(PPh_3)$_3$]$^+$ (m/z 849). The relative intensities of the two peaks at m/z 587 and 849 vary with the voltage applied to B1 (see Discussion). The tandem mass spectrum of ions of m/z 849 with no added collision gas shows considerable loss of a phosphine ligand, and so the ion [Cu(PPh_3)$_3$]$^+$ is unstable. In the presence of argon in the collision cell, the same decomposition occurs, but to a much greater extent. These observations immediately suggest that fast-exchange reactions between different phosphines can be investigated by ESMS.

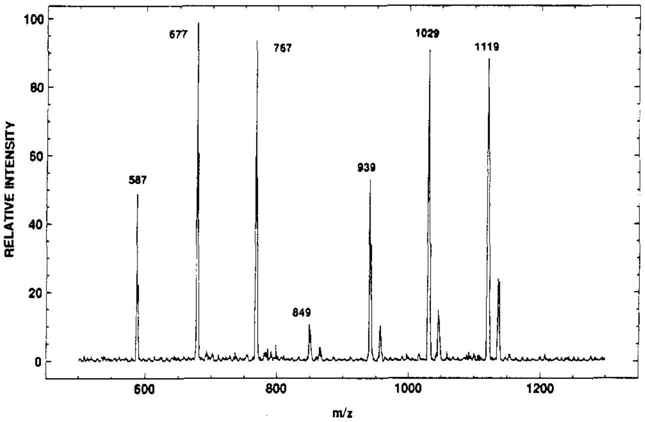

Figure 2. ES mass spectrum of a solution containing [Cu(PPh_3)$_2$]$^+$ + 2 mol of Pom (B1 = 30 V).

Addition of 2 mol equiv of Pom to [Cu(PPh_3)$_2$]$^+$ gives a solution whose phosphorus-31 NMR spectrum shows two sharp resonances, one for each phosphine, confirming that fast exchange is occurring. Figure 2 shows the ES mass spectrum of a solution of the same mixture. It shows peaks due to the ions [Cu(PPh_3)$_2$]$^+$ (m/z 587), [Cu(PPh_3)(Pom)]$^+$ (m/z 677), and [Cu(Pom)$_2$]$^+$ (m/z 767) and others at higher m/z values which are due to [Cu(PPh_3)$_3$]$^+$ (m/z 849), [Cu(PPh_3)$_2$(Pom)]$^+$ (m/z 939), [Cu(PPh_3)(Pom)$_2$]$^+$ (m/z 1029), and [Cu(Pom)$_3$]$^+$ (m/z 1119). The CAD mass spectrum of [Cu(Pom)$_2$]$^+$ gives a product ion at m/z 415, which is [Cu(Pom)]$^+$, while the mixed-phosphine cation [Cu(PPh_3)(Pom)]$^+$ gives the two product ions [Cu(PPh_3)]$^+$ and [Cu(Pom)]$^+$. The ratio of the intensities of the peaks for these product ions is about 1:4, showing that PPh_3 is more readily lost from [Cu(PPh_3)(Pom)]$^+$ than Pom. Similar studies were carried out by adding 2 mol of Pmt and all possible bis- and tris(phosphine)copper

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Table II. Electrospray Mass Spectral Data for Copper Phosphine Cations

compound	ions (ESMS) (*m/z*)
$(PPh_3)_2Cu(BH_4)$	$[Cu(PPh_3)_2]^+$ (587)
$(PPh_3)_2Cu(BH_4)$ + PPh_3	$[Cu(PPh_3)_2]^+$ (587), $[Cu(PPh_3)_3]^+$ (849)
$(PPh_3)_2Cu(BH_4)$ + 2Pmt	$[Cu(PPh_3)_2]^+$ (587), $[Cu(PPh_3)(Pmt)]^+$ (629), $[Cu(Pmt)_2]^+$ (671), $[Cu(PPh_3)_3]^+$ (849), $[Cu(PPh_3)_2(Pmt)]^+$ (891), $[Cu(PPh_3)(Pmt)_2]^+$ (933), $[Cu(Pmt)_3]^+$ (975)
$(PPh_3)_2Cu(BH_4)$ + 2Pom	$[Cu(PPh_3)_2]^+$ (587), $[Cu(PPh_3)(Pom)]^+$ (677), $[Cu(Pom)_2]^+$ (767), $[Cu(PPh_3)_3]^+$ (849), $[Cu(PPh_3)_2(Pom)]^+$ (939), $[Cu(PPh_3)(Pom)_2]^+$ (1029), $[Cu(Pom)_3]^+$ (1119)
$(PPh_3)_2Cu(BH_4)$ + 2Pmt + 2Pom	$[Cu(PPh_3)_2]^+$ (587), $[Cu(PPh_3)(Pmt)]^+$ (629), $[Cu(Pmt)_2]^+$ (671), $[Cu(PPh_3)(Pom)]^+$ (677), $[Cu(Pmt)(Pom)]^+$ (719), $[Cu(Pom)_2]^+$ (767), $[Cu(PPh_3)_3]^+$ (849), $[Cu(PPh_3)_2(Pmt)]^+$ (891), $[Cu(PPh_3)(Pmt)_2]^+$ (933), $[Cu(PPh_3)_2(Pom)]^+$ (939), $[Cu(Pmt)_3]^+$ (975), $[Cu(PPh_3)(Pmt)(Pom)]^+$ (981), $[Cu(Pmt)_2(Pom)]^+$ (1023), $[Cu(PPh_3)(Pom)_2]^+$ (1029), $[Cu(Pmt)(Pom)_2]^+$ (1071), $[Cu(Pom)_3]^+$ (1119)

complexes were again observed; details are given in Table II. It emerges from the CAD spectra that loss of the lighter phosphine is always favored, as was also noted for the bis(phenanthroline) cations. This explains the relative intensities of the peaks due to the bis(phosphine)copper cations in the ES mass spectrum, since collisionally induced decompositions will be occurring in the region of the evaporation nozzle where there is a high concentration of solvent molecules in the gas phase.

A solution was prepared containing 1 mol of $[Cu(PPh_3)_2]^+$, 2 mol of Pom, and 2 mol of Pmt. The phosphorus-31 NMR spectrum showed three resonances of approximately equal intensities, indicating a rapidly exchanging system, as expected. In the ES mass spectrum all six possible bis(phosphine)copper cations were observed in the *m/z* range 587–767, but the relative intensities were again weighted in favor of the heavier phosphines. In the higher mass region associated with the tris(phosphine)-copper cations, most of the possible combinations could be identified, but peaks due to $[Cu(PPh_3)_3]^+$ and $[Cu(PPh_3)_2(Pom)]^+$ were difficult to detect and that due to $[Cu(PPh_3)_2(Pmt)]^+$ (*m/z* 891) was weak, for the reasons discussed above. However, addition of a little extra PPh_3 to the solution, which shifted the statistical distribution slightly in favor of triphenylphosphine complexes, allowed simultaneous observation of all the tris(phosphine)copper cationic species.

Discussion

We have previously reported ES mass spectra of solutions containing several nonexchanging compounds,[12] but this is the first report of an ESMS study on an inorganic system in which species are exchanging ligands at a rate which is fast on the NMR time scale. The enormous advantage of ESMS over NMR spectroscopy in the study of exchange reactions is that the exchange effectively stops immediately as the ions enter the gas phase, and thus all the exchanging species are "frozen" into their identities at the moment of volatilization and can be identified. Obviously, for cases where suitable nuclei are available, e.g. mercury phosphine complexes,[16] NMR spectroscopy can provide much more detailed structural information on the species in solution, and their relative proportions, if slow-exchange spectra can be observed at low temperatures.

For stable ions in nonexchanging systems, the intact ions observed in the gas phase are those preexisting in solution, and we have found that the spectra are relatively insensitive to the B1 voltage. However, it emerges from this work with labile species that collisional decomposition of unstable species occurs in the vicinity of the vaporization nozzle of the ion source, and peaks due to product ions may be the most intense in the ES mass spectrum at higher B1 voltages. This is illustrated in Figure 3, which shows the ES mass spectra of a solution containing $[Cu(PPh_3)_2]^+$ and 1 mol equiv of PPh_3 obtained with different voltages applied to B1. As the voltage is increased, the ions are accelerated more rapidly toward the electrode and undergo more vigorous collisions with solvent molecules, leading to collisional decomposition of the unstable tris(triphenylphosphine)copper cation. When stable ions are observed[10–12] by ESMS, this type of decomposition is minimal, so the fact that it is so frequently observed in this system is a direct reflection of the lability of these ions. Since the relative intensities of the peaks vary with applied voltage, it is clear that the ESMS technique provides only qualitative information on the species present and not quantitative data on the concentrations present.

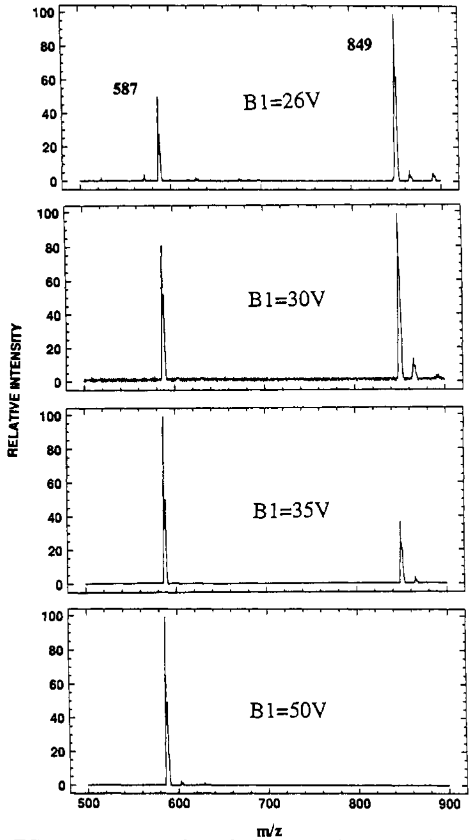

Figure 3. ES mass spectra of a solution containing $[Cu(PPh_3)_2]^+$ + 1 mol of PPh_3 as a function of ion source (B1) voltage.

While NMR spectroscopy can, in many cases, give much more detailed quantitative and structural information than is available from ESMS, the latter will be useful in those situations where NMR spectroscopy is limited or inapplicable, such as paramagnetic systems or those where no suitable NMR nucleus is available, for compounds whose solubility is extremely small, as well as for rapidly exchanging systems such as those described in this work. In general, the combination of ESMS and NMR spectroscopy will be a very powerful tool for the study of most reactions in solution which involve ionic species.

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