

# Investigation of the properties of tris(2-cyanoethyl)phosphine by electrospray and Fourier transform ion cyclotron resonance mass spectrometries†

Keith J. Fisher,\*<sup>a</sup> William Henderson,\*<sup>b</sup> Ian G. Dance<sup>a</sup> and Gary D. Willett<sup>a</sup>

<sup>a</sup> School of Chemistry, University of New South Wales, Sydney, New South Wales, 2052 Australia

<sup>b</sup> Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

The small, ambidentate phosphine  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  (tcp) has been investigated by laser ablation Fourier transform ion cyclotron resonance (LA-FTICR) and electrospray mass spectrometries (ESMS), particularly with regard to its interaction with some alkali- and transition-metal monocations. These two different ionization and mass spectrometric techniques have been shown to be complementary for this phosphine. Complexes of the type  $[\text{M}(\text{tcp})]^+$  ( $\text{M} = \text{H}$  or alkali-metal cation) were observed using both techniques. Corresponding species were observed for  $\text{M} = \text{Cu}$ ,  $\text{Ag}$ ,  $\text{Co}$  and  $\text{Ni}$  using LA-FTICR. In the negative-ion LA spectra the phosphine provides a source of cyanide ions, forming metal-cyanide cluster anions of the type  $[\text{M}_x(\text{CN})_{x+1}]^-$ . These are predominant for  $\text{Cu}$ , and less so for  $\text{Ag}$ ,  $\text{Co}$  and  $\text{Ni}$ . Loss of acrylonitrile from the metal complexes also provides one of the main decomposition pathways which can be observed in both positive- and negative-ion modes, giving complexes of the type  $[\text{M}(\text{CH}_2\text{CHCN})_x]^+$  ( $x = 1$  or  $2$ ) and  $[\text{M}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})\}]^-$  respectively.

Tris(2-cyanoethyl)phosphine,  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  (tcp), is a small, air-stable, and potentially multidentate phosphine ligand, containing hybrid soft (phosphorus) and harder (nitrile) donor groups. It is readily prepared in one step by the reaction of commercially available and inexpensive  $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$  with acrylonitrile,<sup>1</sup> or by direct hydrophosphination of acrylonitrile with  $\text{PH}_3$ .<sup>2</sup> As a result of these desirable characteristics there have been a number of studies on the co-ordination chemistry of tcp, including mononuclear complexes of nickel(0)<sup>3</sup> and nickel(II),<sup>4</sup> platinum(II),<sup>5</sup> mercury(II),<sup>6</sup> chromium(0),<sup>7</sup> molybdenum(0),<sup>7</sup> silver(I)<sup>8</sup> and gold(I).<sup>5,9</sup> Polymeric materials have also been identified, where the tcp ligand can bridge between two metal centres using the phosphine and nitrile groups.<sup>10</sup>

We are interested in using mass spectrometry to probe the properties and co-ordination chemistry of phosphines and other ligands. This has the advantage of allowing studies with very small amounts of material. Once promising systems are identified, these can then act to direct subsequent synthetic studies on the macroscopic scale. Perhaps the classical example of such methodology is the mass spectrometric detection, and subsequent macroscopic isolation, of fullerenes. In this paper, we describe how two different mass spectrometric techniques can be used to probe the co-ordination chemistry of tcp, towards alkali-metal and transition-metal monocations. Both the techniques of production and observation of ions may greatly influence the ions observed and the subsequent study of their properties.

Electrospray mass spectrometry (ESMS) may be used to conveniently ascertain the nature of the ions in solution. It is regarded as a soft ionization technique which transfers ions in solution to ions in the gas phase.<sup>11</sup> Increasing the skimmer cone voltage during ion observation in ESMS experiments is well known to effect the fragmentation of ions,<sup>11</sup> and so dissociation studies can be undertaken during ESMS, but using sector or quadrupole mass spectrometers ion-molecule reactions may not be easily studied. The ion lifetimes in these spectrometers is also short, generally microseconds. However, ion traps such as the Fourier transform ion cyclotron resonance (FTICR) mass spectrometer allow for the storage and further manipulation of ions, generally for periods from milliseconds to seconds. The

use of electrospray with FTICR is not yet common,<sup>12</sup> but ionization of solids using lasers is a common process used with FTICR. The use of lasers to desorb ions from a solid or even to produce ions by ablation may be regarded as a much harsher ionization technique than electrospray. Often the observed ions, especially from non-molecular solids such as metal sulfides, may be formed in the laser plume.<sup>13</sup> The observation of intact molecule ions using laser desorption is possible<sup>14</sup> and the trapping and manipulation of those ions is also possible in FTICR. Laser ablation of metals normally produces the monocations  $\text{M}^+$  which can be observed to react with neutral molecules in the FTICR cell. The laser ablation of a metal in a solid mixture of a potentially co-ordinating ligand has the possibility that unusual products may be observed, as the metal cations may react with neutral donor molecules or the donor molecule ion may react with metal atoms. To the best of our knowledge, FTICR studies on reactions of metal ions with phosphines have only been reported for studies of phosphalkynes.<sup>15,16</sup>

Using two complementary mass spectrometric techniques gives a potentially new insight into the gas-phase chemistry of phosphines and metal adducts. In this study, information on metal-tcp complexes has been ascertained by the technique of laser ablation (LA) FTICR of mixtures of tcp and pure metals or metal salts, and the observed ions compared with those obtained by ESMS. The FTICR studies have also included collision-induced dissociation (CID) experiments of the prominent ions observed after ablation in order to verify the composition of the ions.

## Experimental

The phosphine tcp was prepared by the literature procedure,<sup>1</sup> and the high purity of the product confirmed by <sup>31</sup>P NMR spectroscopy. Commercial graphite, containing some sodium and potassium salt impurities, was used. Metal powders and other metal salts were of reagent grade and used as supplied from commercial sources.

## Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS)

Mass spectra were observed using a Spectrospin CM-47 FTICR

† Non-SI unit employed: bar = 10<sup>5</sup> Pa.

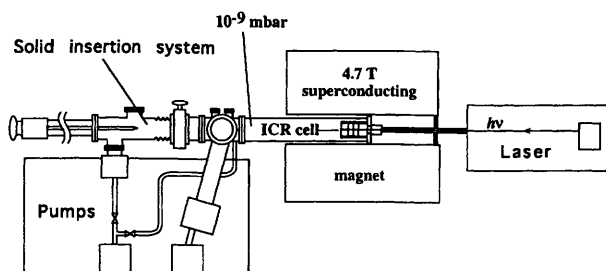


Fig. 1 Schematic diagram of the laser ablation ion cyclotron resonance mass spectrometer

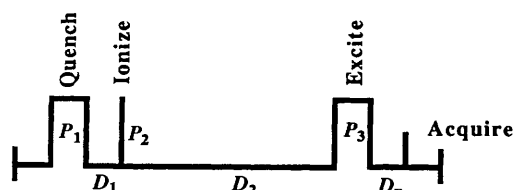


Fig. 2 A typical pulse sequence used for laser ablation

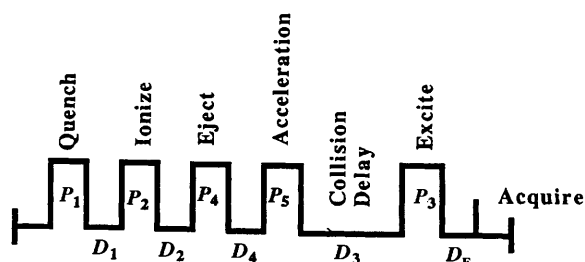


Fig. 3 A typical pulse program used for collision induced dissociation

instrument (shown schematically in Fig. 1). Powdered samples of pure tcp and mixtures of metals or carbon with tcp were pressed into satellite probe tips. Mixtures of tcp:metal ( $\approx 2:1$  w/w) were found to give the best spectra. The probe tip was mounted on the satellite and located on the end of the cell using a solid insertion probe, and the laser (focused to an area of  $\approx 0.01 \text{ mm}^2$ ) pulsed to ionize the sample. In these studies the laser ablation occurred at the same spot on the sample.

A Nd-YAG laser (1064 nm) was used in a Q-switched mode (pulse width 8 ns) giving a range of laser powers ( $40\text{--}260 \text{ MW cm}^{-2}$ ). Most experiments were carried out with a laser power of  $260 \text{ MW cm}^{-2}$ . Ions were trapped for up to 2 s in a cylindrical ICR cell (radius  $30 \times 60 \text{ mm}$ ) with six titanium single-section plates in an ultra high-vacuum chamber maintained at a base pressure of  $10^{-9} \text{ mbar}$  by a turbomolecular pump. Positive ions were trapped in the cell by a potential of  $+3 \text{ V}$  and negative ions by a potential of  $-3 \text{ V}$ . A typical pulse program is shown in Fig. 2. The sequence of events in the laser ablation production of ions was as follows: (1) a quench radiofrequency pulse  $P_1$  ( $5000 \mu\text{s}$ ) used to eject all ions from the cell; (2) a delay  $D_1$  (1 ms) preceding the ionizing laser pulse  $P_2$  (10 ms); (3) a variable reaction delay  $D_2$  (generally 0.1–1 s) used to facilitate the removal of unwanted neutrals produced by the laser; (4) a radiofrequency pulse  $P_3$  used to excite the ions ( $\approx 50 \mu\text{s}$ ); and (5) signal acquisition initiated  $500 \mu\text{s}$  ( $D_E$ ) after the excitation pulse.

Collision induced dissociation spectra were obtained, with argon at  $1 \times 10^{-7} \text{ mbar}$  as the target gas, using the pulse sequence shown in Fig. 3. Similar values of  $P_1\text{--}P_3$ ,  $D_1$  and  $D_2$  were used to those in the laser program. A radiofrequency pulse  $P_4$  was used to eject all unwanted ions leaving only the specific ion or ions for study. After a short delay ( $D_4 = 1 \mu\text{s}$ ) a pulse  $P_5$  (variable between 20 and  $100 \mu\text{s}$ ) with the frequency of the selected ion or ions was used to accelerate the ions in the presence of argon gas. The ions were allowed to collide with argon for a delay time where single collision or a very small

number of collisions occurred ( $D_3 = 0.02\text{--}0.05 \text{ s}$ ). The spectra of the resulting ions were then collected using an excitation pulse  $P_3$ .

The ions observed in the FTICR experiments are summarized in Table 1.

### Electrospray mass spectrometry

The ESMS spectra were recorded in positive-ion mode either on a VG Platform II or a VG Quattro instrument, using MeCN-water (1:1 v/v) as the mobile phase. The tcp was dissolved in a portion of mobile phase to give a solution of approximate concentration  $0.1 \text{ mmol dm}^{-3}$ , and a small quantity of the appropriate metal salt (LiBr, NaCl or KCl) was immediately added. The samples were introduced *via* a microlitre syringe and a  $10 \mu\text{l}$  sample loop fitted to a Rheodyne injector, with the mobile phase being delivered to the mass spectrometer by an LC pump, at a flow rate of  $0.1 \text{ cm}^3 \text{ min}^{-1}$ . Nitrogen was employed both as the nebulizing and drying gas. Fragmentation was investigated by varying the skimmer cone voltage, typically from 10 to 80 V. Spectra were typically acquired as 10 to 12 scans, subsequently averaged. The ions observed in the ESMS experiments are summarized in Table 2.

## Results and Discussion

### FTICR studies on tcp

Laser desorption of pure tcp gave poor positive-ion spectra with only weak  $[\text{Htcp}]^+$  and  $[\text{K(tcp)}]^+$  ions observed. The negative-ion spectra indicated considerable destruction of the tcp molecule with many ions differing by unit mass. In the laser desorption process the tcp molecules absorb all the radiant energy and suffer considerable decomposition. Using a solid matrix system as a radiation absorber may provide heat for the evaporation of the molecule under study. Thus, laser desorption of tcp from a mixture with commercial graphite was used to volatilize the phosphine, *via* heating of the graphite. Similar techniques have been used previously. For example,  $\text{C}_{60}$  has been used with organic and inorganic molecules to act as a radiation absorber resulting in the observation of molecular ions.<sup>17</sup>

The FTICR mass spectrum of the graphite–tcp mixture afforded a number of species, including  $[\text{Htcp}]^+$  ( $m/z$  194),  $[\text{Na(tcp)}]^+$  ( $m/z$  216),  $[\text{K(tcp)}]^+$  ( $m/z$  232),  $[\text{Na(tcpo)}]^+$  ( $m/z$  232) [tcpo = tris(2-cyanoethyl)phosphine oxide] and  $[\text{K(tcpo)}]^+$  ( $m/z$  248), together with an unidentified ion at  $m/z$  284. Later experiments with pure graphite did not give the latter ion. Although an accurate mass was determined for this ion and CID studies gave  $m/z$  60 as the fragment ion, no unambiguous assignment of the formula could be made. The broad-band spectrum is illustrated in Fig. 4. Low-intensity ions were also observed for  $\text{Na}^+$  and  $\text{K}^+$ ; it seems likely that the  $\text{Na}^+$  and  $\text{K}^+$  ions arise from the graphite, which may also be the source of oxygen from which the phosphine oxide (tcpo) has been formed. Collision induced dissociation was employed to verify the nature of the tcp-containing ions. Thus, for example, CID on the  $[\text{Na(tcp)}]^+$  ion afforded  $\text{Na}^+$  ( $m/z$  23). The ions  $[\text{K(tcp)}]^+$  and  $[\text{Na(tcpo)}]^+$  have the same mass-to-charge ratio ( $m/z$  232), however the occurrence of both species is indicated by the CID experiment, which furnished both  $\text{Na}^+$  and  $\text{K}^+$  ions. These results suggest that laser desorption of tcp with an alkali-metal halide might provide strong adduct ions in the gas phase, as described in the next section.

### Laser desorption of tcp and the alkali-metal halides KBr and LiBr

Upon laser desorption of a tcp–KBr mixture the ion  $[\text{K(tcp)}]^+$  was observed as an intense ion at  $m/z$  232, together with a less-

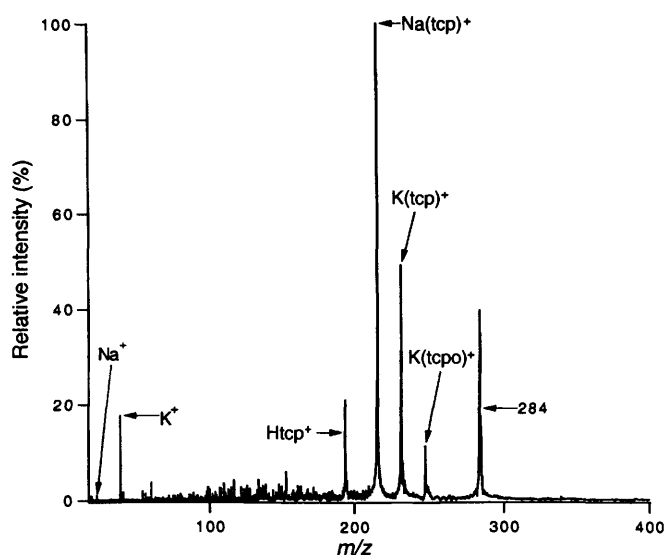


Fig. 4 Positive-ion broad-band spectrum of the laser ablation of a graphite-tcp mixture

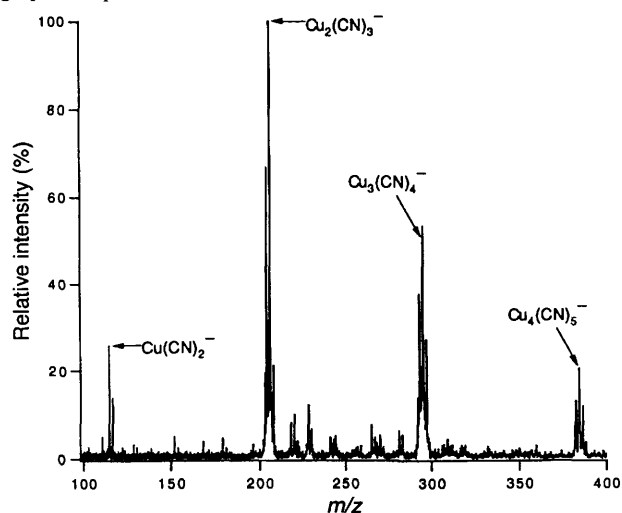


Fig. 5 Negative-ion broad-band spectrum of the laser ablation of a copper metal-tcp mixture

intense ion  $[\text{Htcp}]^+$  ( $m/z$  194) and a number of other species including  $[\text{K}_2\text{Br}]^+$ .

Laser ablation of a mixture of tcp and  $\text{Li}_2\text{CO}_3$  gave  $[\text{Li}(\text{tcp})]^+$  as the predominant ion at  $m/z$  200. The CID experiments suggested that this ion was very stable (as might be predicted for complexes of the high-charge-density  $\text{Li}^+$  ion), though the decomposition ion  $\text{Li}^+$  fell outside the detector range of the FTICR mass spectrometer. A similar high stability of lithium ion adducts of polyglycols has been observed previously.<sup>18</sup>

#### Laser ablation of tcp with copper or silver metal powders

Laser irradiation of a mixture of a metal powder with the phosphine achieves a dual role; heating of the substrate volatilizes the phosphine ligand, while providing a source of  $\text{M}^+$  ions, which may subsequently complex with the ligand. For both Cu and Ag, the predominant metal-ligand species in the positive-ion spectra were the complex ions  $[\text{M}(\text{tcp})]^+$ , observed at  $m/z$  256/258 (Cu) and 300/302 (Ag). A weak ion due to  $[\text{Cu}(\text{tcp})_2]^+$  was also observed at  $m/z$  449/451. Other species can be tentatively identified as containing acrylonitrile ligands, for example  $[\text{Cu}(\text{CH}_2\text{CHCN})]^+$  at  $m/z$  116/118 and  $[\text{Cu}(\text{CH}_2\text{CHCN})_2]^+$  at  $m/z$  169/171. The acrylonitrile complex  $[\text{Cu}(\text{CH}_2\text{CHCN})]^+$  has been previously suggested to have a side-on  $\pi$ -bonded structure, co-ordinated to both the alkene and nitrile moieties.<sup>19</sup> The CID of the  $[\text{Cu}(\text{tcp})]^+$  ion gave

predominantly  $\text{Cu}^+$  ions, together with  $[\text{Cu}(\text{CH}_2\text{CHCN})]^+$  at  $m/z$  116/118.

The negative-ion spectrum of an ablated Cu-tcp mixture, Fig. 5, was rather simpler than the corresponding positive-ion spectrum. Copper(I) cyano clusters, of the type  $[\text{Cu}_x(\text{CN})_{x+1}]^-$ , were observed up to  $x = 4$ ; the isotope patterns of these ions match the theoretical isotope patterns as shown for  $[\text{Cu}_3(\text{CN})_4]^-$  in Fig. 6. The CID experiments confirmed the interrelationship of the various clusters with loss of  $\text{CuCN}$  being the pathway of decomposition:  $[\text{Cu}_4(\text{CN})_5]^- \rightarrow [\text{Cu}_3(\text{CN})_4]^- \rightarrow [\text{Cu}_2(\text{CN})_3]^- \rightarrow [\text{Cu}(\text{CN})_2]^- \rightarrow \text{CN}^-$ . Low-intensity ions at  $m/z$  228 and 230 are tentatively assigned as the species  $[\text{Cu}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^+$ .

Similar results were obtained in the negative-ion spectrum of a silver-tcp mixture, though with some significant differences. Silver-cyano cluster anions were also observed, but to a lesser extent than with copper, *i.e.*  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Ag}_2(\text{CN})_3]^-$  were observed, but not higher homologues. The CID of the ions due to  $[\text{Ag}(\text{CN})_2]^-$  ( $m/z$  159, 161) furnished the expected  $\text{CN}^-$  ion at  $m/z$  26. The ion  $[\text{Ag}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ , analogous to the copper species, was also observed at  $m/z$  272, 274. Other ions observed were  $[\text{P}(\text{CN})\text{CH}_2\text{CH}_2\text{CN}]^-$  ( $m/z$  111) and  $[\text{C}_4\text{CN}]^-$  ( $m/z$  74); the latter ion has been observed in the laser ablation spectra of metal cyanides.<sup>20</sup> Both  $[\text{P}(\text{CN})\text{CH}_2\text{CH}_2\text{CN}]^-$  and  $[\text{C}_4\text{CN}]^-$  gave  $\text{CN}^-$  upon CID. Neither of these ions was observed in the analogous copper negative-ion spectrum.

In these negative-ion experiments acrylonitrile thus appears to act as a source of the cyanide ion; identical cyano clusters have been previously reported in laser ablation studies starting from the parent metal(I) cyanides, *viz.*  $\text{CuCN}$  and  $\text{AgCN}$ .<sup>21</sup> It is expected that loss of acrylonitrile from tcp would be one of the major decomposition pathways for a ligand of this type. In a similar manner the P-C bonds of hydroxymethyl-phosphines and -phosphonium salts are also readily cleaved;<sup>22</sup> these are similar materials to the (cyanoethyl)phosphines in that they can both be synthesized by hydrophosphination (of formaldehyde<sup>23</sup> or acrylonitrile<sup>2</sup> respectively). In analogous fashion, (cyanoethyl)phosphonium salts can also be converted under mild basic conditions into the corresponding phosphine, by loss of acrylonitrile.<sup>24</sup> This illustrates the similarities between these two types of materials.

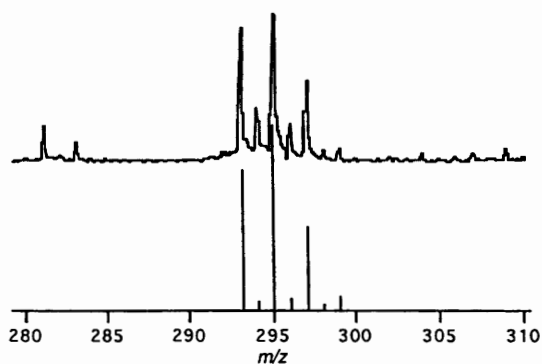
#### Laser ablation of tcp with cobalt or nickel metal powders

The positive-ion spectrum of an ablated Co-tcp mixture contained  $[\text{Co}(\text{tcp})]^+$  as a significant ion, the other major ions being  $[\text{Co}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^+$  and  $[\text{Htcp}]^+$ . Similarly, the positive-ion spectrum of an ablated Ni-tcp mixture gave  $[\text{Ni}(\text{tcp})]^+$  together with  $[\text{Ni}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^+$  and  $[\text{Htcp}]^+$ .

The negative-ion spectrum of ablated cobalt metal with tcp contained  $[\text{Co}(\text{CN})_2]^-$  as the most intense ion; CID on this ion gave the expected  $\text{CN}^-$ . The higher cluster  $[\text{Co}_2(\text{CN})_3]^-$  was also observed at  $m/z$  196, with CID giving  $[\text{Co}(\text{CN})_2]^-$  and  $\text{CN}^-$ . A medium-intensity ion at  $m/z$  224 was tentatively assigned as  $[\text{Co}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ , analogous to the species observed with Cu and Ag; CID on this ion gave  $\text{CN}^-$  and  $[\text{Co}(\text{CN})_2]^+$ . An ion at  $m/z$  222 in the original negative-ion spectrum may be due to a dehydrogenated product, *e.g.*  $[\text{Co}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})(\text{CH}=\text{CHCN})\}]^-$ . Similar anionic species, *viz.*  $[\text{Ni}(\text{CN})_2]^-$  and  $[\text{Ni}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$  were detectable in the negative-ion spectrum of the ablated nickel powder-tcp mixture.

#### Electrospray mass spectrometry

This is a relatively recent ionization technique which has been successfully applied to the characterization of a wide range of biochemical materials. Applications to inorganic chemistry (including compounds such as organophosphines which are



**Fig. 6** Part of the negative-ion broad-band spectrum formed by laser ablation of a copper metal–tcp mixture, showing the  $[\text{Cu}_3(\text{CN})_4]^-$  ion and the calculated isotope pattern

widely used as ligands) are much fewer,<sup>25</sup> though there is considerable current interest in the development of applications in inorganic chemistry. The ESMS technique is generally considered to transfer existing solution ions into the gas phase, whence they can be separated and analysed. Furthermore, the ionization technique is soft in nature, often resulting in zero or minimum fragmentation of the parent ions (particularly when the ions under investigation bear a single positive or negative charge). For neutral molecules which bear basic oxygen or

nitrogen atoms, these readily form protonated  $[\text{MH}]^+$  ions, or adducts with alkali-metal cations. We have already demonstrated the affinity of tcp for alkali-metal cations by FTICR. Thus, tcp gave a strong  $[\text{Htcp}]^+$  ion at relatively high cone voltages (70 V). At lower cone voltages (20 V) ammonium ion adducts are observed, such as  $[\text{NH}_4(\text{tcp})]^+$ , others being indicated in Table 2. Presumably these arise as a result of hydrogen bonding between the  $\text{NH}_4^+$  ion and nitrile groups. It is worth noting that phosphines which do not contain basic O or N atoms typically give weak adduct ions with  $\text{H}^+$  and/or  $\text{NH}_4^+$  on account of the low basicity of the phosphorus centre. For such compounds, however, ionization can be readily effected by addition of silver nitrate, which generates cationic silver(I) phosphine complexes *in situ*.<sup>26</sup>

The ESMS spectra of tcp recorded with added alkali-metal cations ( $\text{M}^+$ ) also gave strong positive-ion spectra, with  $[\text{M}(\text{tcp})]^+$  being a dominant ion observed, particularly at higher cone voltages. At lower cone voltages (e.g. 20 V) other ions were often discernible, including  $[\text{M}(\text{tcp})_2]^+$ , and for  $\text{Li}^+$  the ion  $[\text{Li}(\text{tcp})(\text{MeCN})]^+$ . The alkali-metal cations also form acetonitrile-solvated ions, such as  $[\text{K}(\text{MeCN})_2]^+$  and  $[\text{Li}(\text{MeCN})_3]^+$ . This is illustrated by the positive-ion spectrum of tcp with added  $\text{Li}^+$ , shown in Fig. 7. These observations, together with the observation of a strong  $[\text{Htcp}]^+$  ion in the absence of added metal ions, suggest that it is the nitrile functionalities of the tcp which are involved in the ES ionization process.

**Table 1** The FTICRMS data for tcp and mixtures of it with graphite or metal powders

| System                         | Ion mode | Ions ( $m/z$ )  | CID ions ( $m/z$ )   |
|--------------------------------|----------|---|--|
| tcp                            | Positive | $[\text{Htcp}]^+$ (194)<br>$[\text{K}(\text{tcp})]^+$ (232)   |  |
| C + tcp                        | Positive | $[\text{Htcp}]^+$ (194)<br>$[\text{Na}(\text{tcp})]^+$ (216)<br>$[\text{Na}(\text{tcpo})]^+ / [\text{K}(\text{tcp})]^+$ (232)<br>$[\text{K}(\text{tcpo})]^+$ (248)<br>Unidentified (284)  | $\text{Na}^+$ (23)<br>$\text{Na}^+$ (23), $\text{K}^+$ (39)  |
| $\text{Li}_2\text{CO}_3$ + tcp | Positive | $[\text{Li}(\text{tcp})]^+$ (200)   | (60)<br>$[\text{Li}(\text{tcp}) - 3\text{H}]^+$ (197)<br>$[\text{Li}(\text{tcp}) - \text{CH}_2\text{CHCN}]^+$ (147)<br>$[\text{Li}(\text{tcp}) - \text{CH}_2\text{CHCN} - \text{H}]^+$ (146)<br>$[\text{Li}(\text{CH}_2\text{CHCN})]^+$ (60) |
| KBr + tcp                      | Positive | $[\text{K}(\text{PCH}_2\text{CH}_2\text{CN})]^+$ (124)<br>$[\text{Htcp}]^+$ (194)<br>$[\text{K}(\text{tcp})]^+$ (232)   | $\text{K}^+$ (39)  |
| Cu + tcp                       | Positive | $[\text{Cu}(\text{CH}_2\text{CHCN})]^+$ (116/118)<br>$[\text{Cu}(\text{CH}_2\text{CHCN})_2]^+$ (169/171)<br>$[\text{Cu}(\text{tcp})]^+$ (256/258)<br>$[\text{Cu}(\text{tcp})(\text{CH}_2\text{CHCN})]^+$ (309/311)  | (116/118) and $\text{Cu}^+$ (63/65)  |
|                                | Negative | $[\text{Cu}(\text{CN})_2]^-$ (115/117)<br>$[\text{Cu}_2(\text{CN})_3]^-$ (204/206/208)<br>$[\text{Cu}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ (228/230)<br>$[\text{Cu}_3(\text{CN})_4]^-$ (293/295/297/299)<br>$[\text{Cu}_4(\text{CN})_5]^-$ (382/384/386/388/390) | (115/117)<br>(204/206/208), (115/117)<br>(293/295/297/299), (204/206/208), (115/117)   |
| Ag + tcp                       | Positive | $\text{Ag}^+$ (107, 109)<br>$[\text{Ag}(\text{tcp})]^+$ (300, 302)  |  |
|                                | Negative | $\text{C}_4\text{CN}^-$ (74)<br>$[\text{P}(\text{CN})\text{CH}_2\text{CH}_2\text{CN}]^-$ (111)<br>$[\text{Ag}(\text{CN})_2]^-$ (159, 161)<br>$[\text{Ag}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ (272, 274)<br>$[\text{Ag}_2(\text{CN})_3]^-$ (292/294/296)         | (26) ( $\text{CN}^-$ )<br>(26)<br>(26)   |
| Co + tcp                       | Positive | $[\text{Co}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^+$ (198)<br>$[\text{Htcp}]^+$ (194)<br>$[\text{Co}(\text{tcp})]^+$ (252)  |  |
|                                | Negative | $[\text{Co}(\text{CN})_2]^-$ (111)<br>$[\text{Co}_2(\text{CN})_3]^-$ (196)<br>$[\text{Co}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})(\text{CH}=\text{CHCN})\}]^-$ (222)<br>$[\text{Co}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ (224)                     | $\text{CN}^-$ (26)<br>(111), (26)<br>(26), (111), $[\text{Co}(\text{CN})(\text{CH}_2\text{CN})]^-$ (125),<br>$[\text{Co}(\text{CN})\{\text{P}(\text{HCH}_2\text{CH}_2\text{CN})\}]^-$ (171)  |
| Ni + tcp                       | Positive | $[\text{Htcp}]^+$ (194)<br>$[\text{NiP}(\text{CH}_2\text{CH}_2\text{CN})_2]^+$ (197)<br>$[\text{Ni}(\text{tcp})]^+$ (251)   |  |
|                                | Negative | $[\text{Ni}(\text{CN})_2]^-$ (110)<br>$[\text{Ni}(\text{CN})\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2\}]^-$ (223)   |  |

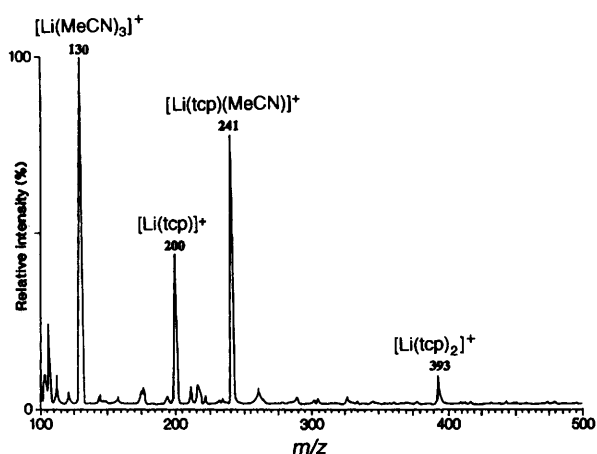


Fig. 7 Positive-ion electrospray spectrum (cone voltage 20 V) of a solution of tcp with added LiBr

Table 2 Positive-ion ESMS data for tcp solutions

| Mixture    | Cone voltage (V) | Ions ( <i>m/z</i> )   |
|------------|------------------|---|
| tcp        | 20               | [NH <sub>4</sub> (tcp) <sub>2</sub> ] <sup>+</sup> (404), [NH <sub>4</sub> (tcp)] <sup>+</sup> (211), [NH <sub>4</sub> (MeCN) <sub>2</sub> ] <sup>+</sup> (100), [NH <sub>4</sub> (MeCN)] <sup>+</sup> (59) |
|            | 70               | [Htcp] <sup>+</sup> (194)   |
| tcp + NaCl | 20               | [Na(tcp)] <sup>+</sup> (216), [Na(MeCN) <sub>2</sub> ] <sup>+</sup> (105)   |
| tcp + LiBr | 20               | [Li(tcp) <sub>2</sub> ] <sup>+</sup> (393), [Li(tcp)(MeCN)] <sup>+</sup> (241), [Li(tcp)] <sup>+</sup> (200), [Li(MeCN) <sub>3</sub> ] <sup>+</sup> (130)   |
|            | 50               | [Li(tcp)] <sup>+</sup> (200)  |
| tcp + KCl  | 20               | [K(tcp) <sub>2</sub> ] <sup>+</sup> (425), [K(tcpo)] <sup>+</sup> (248), [K(tcp)] <sup>+</sup> (232), [K(MeCN) <sub>2</sub> ] <sup>+</sup> (121)  |

In summary, we have shown by laser ablation FTICR and ESMS that alkali-metal cations interact strongly with tcp. The stability of these adducts is attested to by the collision-induced dissociation experiments carried out in the FTICR mass spectrometer. Copper, silver, cobalt and nickel also produce [M(tcp)]<sup>+</sup> ions, but in the negative-ion spectra the production of metal-cyanide ions appears to be the predominant pathway. We have shown that two very different mass spectrometric techniques, with different ionization methods, have yielded similar results from both the solid and solution states. Other studies on phosphines and metal-phosphine systems are in progress.

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