The Adduct between Triphenyl Phosphine and Triphenyl Phosphine Telluride. A Tellurium(0) Compound

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Tetraphenylarsionium tellurocyanate reacts with excess triphenyl phosphine in acetonitrile in the presence of lithium perchlorate to form a bright yellow compound in high yield. This compound, which is very stable in the solid state, is shown to be the adduct between triphenyl phosphine and triphenyl phosphine telluride.

An X-ray structure determination of the adduct reveals that all tellurium atoms and phosphorus atoms lie on threefold axes and each formula unit contains a linear P–Te–P configuration. The results show that in the linear P–Te–P configuration there is a "normal" bond between tellurium and one of the phosphorus atoms, while the interaction between tellurium and the other phosphorus atom is rather weak. IR and Raman spectra of the adduct are presented and complement the X-ray studies regarding the general shape of the molecule.

It is concluded that the adduct may be regarded as a tellurium(0) compound and the structural similarity with isoelectronic species like the trihalide anions is discussed.

The reactions of tervalent phosphorus compounds with oxygen, sulfur, and selenium and the products from these reactions have been investigated in great detail for over a century. The reaction of phosphines and related compounds with tellurium and the corresponding phosphine tellurides appear to be far less known.

The first known organophosphorus compound with a phosphorus-tellurium bond was made by Foss.1 He noted that finely divided tellurium dissolved on gentle heating in an ethanol solution of potassium diethyl phosphite to give the corresponding telluroposphate. The colourless hygroscopic needles, rapidly darkening in moist air, were found to be less stable than the corresponding thio and seleno salts.2

Gryszkiewicz-Trochimowski and co-workers3 found similarly that tellurium dissolved in a benzene solution of diethyl ethylphosphonite to give a red solution. The product, however, decomposed readily on attempted purifica-
tion by distillation. Allyl diethyl phosphononite, on the other hand, is known to
give a distillable tellurophosphonate.4

In recent years, Zingaro and co-workers have made a number of phosphine
tellurides from the corresponding phosphines and finely divided tellurium.5–7
Several of the phosphine tellurides have been found to be sufficiently stable to
allow elemental analysis and IR studies to be performed.7,8 Likewise, tris-
dimethylamino phosphine9,10 and N-diphenylphosphino triphenylphospha-
zene11 have been found to react readily with tellurium to give crystalline
products. The dipole moment of trioctyl phosphine telluride12 has been
determined and found to be of the same order of magnitude as that of the corre-
spending sulfide and selenide. A review on phosphorus chalcogenides has
ercently been published.13

According to Zingaro,6 tellurium dissolves in toluene solutions of trialkyl
phosphines, arylidialkyl phosphines and, although to a very limited extent, in
alkyldiaryl phosphines. No alkyl diaryl phosphine tellurides appear to have
been reported. Elemental tellurium was found not to dissolve in solutions of
triphenyl phosphine. Interestingly, a similar reactivity pattern of these phos-
phines is observed in their reaction with carbon disulfide; trialkyl phosphines
and arylidialkyl phosphines form adducts easily with this substrate, while the
other two members in this series do not.14 The smooth increase in hydrogen
basicity from triphenyl phosphine to trialkyl phosphine15 suggests that the
hydrogen basicities of the various tervalent phosphorus compounds are a poor
measure of the ability of these compounds to form adducts with very polariz-
able Lewis acids. This view is supported by the facile formation of telluro-
phosphonates from the weakly basic dialkyl alkyldiphosphonites and tellurium.3,4

The differing and mainly negative temperature coefficients of the solubility
of tellurium in the various phosphines6 indicate that the formation of phos-
phine tellurides is thermodynamically controlled. The formation of phosphine
tellurides may not be directly connected with the generally accepted nucleo-
philicities of the phosphorus compounds, as has been suggested.5,13

As an equilibrium mixture is obtained from the reaction between tellurium
and tervalent phosphorus compounds,6 an improvement to the synthesis of
phosphine tellurides would be to use a reagent containing tellurium, but with
a leaving group of lower tellurium basicity. Potassium selenocyanate has been
used successfully in the facile synthesis of triaryl phosphine selenides,16 sug-
gesting the cyanide ion to be a poorer selenium base than is a triaryl phosphate.
Similarly, from the unstable nature of the tellurocyanate ion,18 the tellurium
basicity of the cyanide ion appears to be low and a salt of the tellurocyanate
ion was therefore tried as a reagent toward triphenyl phosphine.

When a four- or fivefold excess of triphenyl phosphine was added to a solu-
tion of tetr phenylarsenium tellurocyanate in purified acetonitrile, a very
slight increase of the yellow colour of the solution was observed. The IR of the
solution, however, showed that the amount of ionic tellurocyanate was un-
changed and no products could be detected after work-up of the solution.
Increasing the reaction time, up to several hours, even at 40°C, did not cause
any reaction, except that the solution turned slightly brownish, presumably
due to traces of elemental tellurium. Using un purified acetonitrile, the solu-
tion turned rapidly cream yellow and on evaporation of the solvent, a yellow
product crystallized among unreacted reactants.
Previously, it has been shown that tetr phenyl arsonium and tetramethylammonium selenocyanate react with triphenyl phosphine in purified acetonitrile to give a quantitative yield of triphenyl phosphine selenide provided traces of hard Lewis acids, like acetic acid or lithium perchlorate, were present. On adding a small amount of lithium perchlorate to an acetonitrile solution of ionic tellurocyanate with triphenyl phosphine in excess, the solution turned instantaneously cream yellow and a yellow crystalline compound could be isolated.

Contrary to the reaction with an ionic selenocyanate and triphenyl phosphine where a quantitative yield of triphenyl phosphine selenide is obtained with only minute quantities of lithium perchlorate present, the reaction between ionic tellurocyanate and triphenyl phosphine was found not to be quantitative, as an IR of the reaction mixture still showed a peak due to ionic tellurocyanate at $2081\ \text{cm}^{-1}$ even after prolonged periods.

The dependence upon the amount of lithium perchlorate was examined by slowly adding various amounts of lithium perchlorate to 20 ml solution, containing 1 g tetr phenyl arsonium tellurocyanate, 1.86 mmol, and 2 g triphenyl phosphine, 7.64 mmol, and measuring the amount of unreacted ionic tellurocyanate. As each drop of lithium perchlorate entered the reaction mixture, a greyish colour was formed which disappeared immediately upon stirring. Addition of lithium perchlorate to an acetonitrile solution of tetr phenyl arsonium tellurocyanate, without triphenyl phosphine being present, causes an immediate precipitation of elemental tellurium. The results are listed in Table 1.

<table>
<thead>
<tr>
<th>[Ph₃P]</th>
<th>[LiClO₄]</th>
<th>[TeCN⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.382</td>
<td>0</td>
<td>0.093</td>
</tr>
<tr>
<td>0.35</td>
<td>0.00454</td>
<td>0.068</td>
</tr>
<tr>
<td>0.32</td>
<td>0.00833</td>
<td>0.060</td>
</tr>
<tr>
<td>0.30</td>
<td>0.0462</td>
<td>0.039</td>
</tr>
<tr>
<td>0.28</td>
<td>0.0789</td>
<td>0.018⁴</td>
</tr>
<tr>
<td>0.26</td>
<td>0.107</td>
<td>0.008⁴</td>
</tr>
</tbody>
</table>

These values are approximate as the product started to separate.

The results indicate clearly that even in an excess of lithium perchlorate, some ionic tellurocyanate is unaffected by triphenyl phosphine.

Elemental analysis showed the yellow product to consist of one molecule of triphenyl phosphine telluride together with one molecule of triphenyl phosphine, and not to be triphenyl phosphine telluride itself. The compound decomposed immediately with the formation of elemental tellurium when dissolved in acetonitrile, benzene, acetone, or diethyl ether. When these solvents contained a large amount of triphenyl phosphine, the compound could

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be crystallized without any trace of decomposition. Acetone was found to be the most suitable solvent since it allowed a considerable amount of the product to crystallize prior to the precipitation of triphenyl phosphine. Even in this solvent great care was necessary during the recrystallization, as the low stability of the compound in warm acetone containing triphenyl phosphine in various amounts precluded the use of heat to dissolve the product in a small amount of solvent. The solid product was very stable, and could be stored for long periods in sun-light or moist air without any visible signs of formation of elemental tellurium. The temperature of decomposition was found to be slightly above that of the melting point of triphenyl phosphine.

When excess tetraphenylarsenion cyanide was added to a solution of the compound in acetonitrile containing excess triphenyl phosphine, the colour disappeared immediately, and the required amount of ionic tellurocyanate was formed. These results indicate that the following equilibrium is displaced completely to the left when pure acetonitrile is employed as solvent:

\[ \text{NCTe}^- + 2\text{Ph}_3\text{P} \rightleftharpoons (\text{Ph}_3\text{P})_2\text{Te} + \text{CN}^- \]

The yellow crystalline compound appeared as hexagonal prisms. The space group, from oscillation and Weissenberg photographs, was found to be either \( P3 \) (No. 143) or \( P\bar{3} \) (No. 147). Using MoK\(_\alpha1\) radiation (\( \lambda = 0.70926 \) Å), the unit cell dimensions, with standard deviations in parenthesis, were found to be, \( a = 14.455(8) \) Å, \( c = 12.714(10) \) Å. With three formula units in the unit cell, the calculated density was 1.412 g cm\(^{-3}\). The observed density was 1.40 ± 0.02 g cm\(^{-3}\), determined by flotation in a mixture of 1,4-dibromobutane and a fairly concentrated solution of triphenyl phosphine in benzene. Due to the viscosity of this mixture and the solubility of the adduct, the accuracy in the observed density is somewhat limited.

Pseudo extinctions in \( hkl \) for \( h - k \neq 3n \) indicate that all tellurium and phosphorus atoms lie on threefold axes, and thus that each formula unit (associated with a threefold axis) contains a linear \( P - \text{Te} - P \) configuration. A full X-ray structure determination has been carried out. The results have shown that in the linear \( P - \text{Te} - P \) configuration there is a "normal" bond between tellurium and one of the phosphorus atoms, while the interaction between tellurium and the other phosphorus atom is rather weak. Because of disorder in the structure, with alternating positions for the tellurium atoms, six crystallographically independent "normal" \( \text{Te} - P \) bond lengths have been observed, instead of three bond lengths, as would be observed for an ordered structure. In Table 2 are listed the observed bond lengths, where the tellurium atoms marked with a prime refer to the tellurium atoms of smallest occupancy. Full details of the structure will be reported later.

Due to the disorder in the structure it appears difficult to compare the long \( P - \text{Te} \) interactions and the short \( P - \text{Te} \) bonds with the sum of the van der Waals radii, 3.86 Å,\(^{19}\) and the covalent single bond radii, 2.42 Å,\(^{19}\) respectively. As no structure determinations of organophosphorus tellurides appear to have been performed, one cannot say whether the observed short \( P - \text{Te} \) bond lengths are longer or shorter than in pure phosphine tellurides.

The infrared spectra of triphenyl phosphine, \( \text{Ph}_3\text{P} \), and the adduct between triphenyl phosphine and triphenyl phosphine telluride, \( (\text{Ph}_3\text{P})_2\text{Te} \), were,
A TELLURIUM(0) COMPOUND

Table 2. Tellurium-phosphorus distances in the adduct between triphenyl phosphine and triphenyl phosphine telluride. Standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Short distances (Å)</th>
<th>Long distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te(1) – P(1) = 2.388(11)</td>
<td>Te(1) – P(2) = 3.412(11)</td>
</tr>
<tr>
<td>Te(1') – P(2) = 2.424(17)</td>
<td>Te(1') – P(1) = 3.376(18)</td>
</tr>
<tr>
<td>Te(2) – P(3) = 2.381(9)</td>
<td>Te(2) – P(4) = 3.413(11)</td>
</tr>
<tr>
<td>Te(2') – P(4) = 2.270(18)</td>
<td>Te(2') – P(3) = 3.523(17)</td>
</tr>
<tr>
<td>Te(3) – P(5) = 2.278(14)</td>
<td>Te(3) – P(6) = 3.948(12)</td>
</tr>
<tr>
<td>Te(3') – P(6) = 2.373(12)</td>
<td>Te(3') – P(5) = 3.853(14)</td>
</tr>
</tbody>
</table>

as would be expected, very similar in many respects. Vibrations due to phenyl groups are identical in both cases, and are not repeated here. The X-sensitive vibrations of Ph₃P and their counterparts in (Ph₃P)₂Te are recorded in Table 3 together with the appropriate assignments. It is seen that the two sets of data are very similar in each case, but that there are slight differences indicating the effects of heavy tellurium atoms co-ordinated to the Ph₃P moiety. The observed shift to higher frequencies of the ₉ and ₁ modes in co-ordination of Ph₃P is in accordance with the findings by Deacon and Green. The X-sensitive peaks arising from (Ph₃P)₂Te are slightly broader than those from Ph₃P which may suggest some small amount of dissociation, even though this is not apparent from an inspection of the disc.

Table 3. X-Sensitive bands (cm⁻¹).

<table>
<thead>
<tr>
<th>Ph₃Pᵃ</th>
<th>Ph₃Pᵇ</th>
<th>(Ph₃P)₂Teᵇ</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1089</td>
<td>1090</td>
<td>1096</td>
<td>₉</td>
</tr>
<tr>
<td>512</td>
<td>514</td>
<td>513</td>
<td>y</td>
</tr>
<tr>
<td>497</td>
<td>500</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>489</td>
<td>491</td>
<td>491</td>
<td></td>
</tr>
<tr>
<td>433</td>
<td>431</td>
<td>441</td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>420</td>
<td>431</td>
<td>₁</td>
</tr>
<tr>
<td>254</td>
<td>249</td>
<td>249</td>
<td>u</td>
</tr>
<tr>
<td>248</td>
<td>215</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td>187</td>
<td>196</td>
<td>196</td>
<td>x</td>
</tr>
<tr>
<td>186</td>
<td>183</td>
<td>183</td>
<td></td>
</tr>
</tbody>
</table>

ᵃRef. 21. ᵃThis work.

There are, however, three peaks in (Ph₃P)₂Te which are not observed in Ph₃P; these are at 528 (s), 318 (b) and 226 (m) cm⁻¹. Since they cannot be due to either the C₆H₅ or C₃P fragments they presumably arise from the P₂Te part of the molecule.

The Raman spectrum of (Ph₃P)₂Te shows much primary scattering, presumably due to the heavy Te atoms. Nevertheless it is in general agreement with the above and, in particular, confirms the presence of a peak at 530 cm⁻¹.

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not observed in \( \text{Ph}_2 \text{P} \). It was not possible to measure the Raman spectrum of \((\text{Ph}_3 \text{P})_2 \text{Te}\) below 400 cm\(^{-1}\).

If we regard this \( \text{P}_2 \text{Te} \) skeleton as a triatomic molecule then we would expect three fundamental vibrations if it were either angular or linear (although one of these vibrations would be doubly degenerate in the latter case). However, as a linear molecule the formula seems to imply that \( \text{P}_2 \text{Te} \) would be centrosymmetric, whereas the coincidence of a peak (at 528 cm\(^{-1}\)) in the infrared and Raman spectra excludes such a possibility; further, only two fundamental vibrations would be active in the infrared region for a \( \text{P}_2 \text{Te} \) micro-symmetry of \( D_{\infty h} \).

Nevertheless we can assume that the three vibrations observed arise from the \( \text{P}_2 \text{Te} \) skeleton alone or in conjunction with the associated phenyl groups, and indeed it is difficult to suggest an alternative origin for the peaks. They are relatively strong peaks and it is not easy to account for them as combination bands or overtones. In any case we conclude that these are fundamental vibrations, and, in view of the above, the framework of the molecule is presumably angular or, if linear, not centro-symmetric. This latter case, although not established unequivocally by these infrared data, complements the X-ray studies regarding the general shape of the molecule. Similar coincidences between infrared and Raman spectra have been observed in the spectra of the linear trihalide ions, \( \text{XY}_2^- \), which might also have been assumed to be centro-symmetric.\(^{22} \)

The P=O stretching frequency occurs at 1195 cm\(^{-1}\) in triphenylphosphine oxide,\(^{23} \) and Chittenden and Thomas\(^{24} \) have assigned peaks in the ranges 769–685 and 596–532 cm\(^{-1}\) to P=S frequencies, and 577–517 and 535–473 cm\(^{-1}\) to P=Se frequencies. It is possible, therefore, that the peak at 528 cm\(^{-1}\) in the present compound is essentially a P=Te stretching frequency, in which case the other peaks correspond to adduct vibrations or to Te–P–Te modes. Adams\(^{25} \) quotes M–P stretching frequencies in the range 460–180 cm\(^{-1}\) for various phosphine complexes. In Table 4 are collected some representative stretching frequencies of some phosphorus chalcogenides.

<table>
<thead>
<tr>
<th>( \text{R}_2 \text{PX} )</th>
<th>X = O</th>
<th>X = S</th>
<th>X = Se</th>
<th>X = Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ph}_3 \text{PX} )</td>
<td>1195(^e)</td>
<td>637(^c)</td>
<td>562(^e,d)</td>
<td>528(^e)</td>
</tr>
<tr>
<td>(Me(_2)N)(_2)PX</td>
<td>1210(^f)</td>
<td>565(^f)</td>
<td>530(^f)</td>
<td>519(^f)</td>
</tr>
<tr>
<td>(CH(_3))(_2)PX</td>
<td>1172</td>
<td>570</td>
<td>441</td>
<td></td>
</tr>
<tr>
<td>(n-C(_4)H(_9))(_2)PX</td>
<td>1169</td>
<td>596, 583</td>
<td>496</td>
<td>445, 400</td>
</tr>
<tr>
<td>(n-C(_5)H(_11))(_2)PX</td>
<td>1143</td>
<td>599, 588</td>
<td>507</td>
<td>467, 404</td>
</tr>
<tr>
<td>(c-C(_6)H(_11))(_2)PX</td>
<td>1143</td>
<td>619</td>
<td>543</td>
<td>518</td>
</tr>
<tr>
<td>(c-C(_6)H(_11))(_2)PX</td>
<td>1143</td>
<td>727(^f)</td>
<td>685(^e)</td>
<td></td>
</tr>
<tr>
<td>CH(_3)P(X)Cl(_3)</td>
<td>1270(^e)</td>
<td>670(^e)</td>
<td>553(^e)</td>
<td></td>
</tr>
<tr>
<td>CH(_3)P(X)(OC(_2)H(_5))(_2)</td>
<td>1250(^e)</td>
<td>591(^e)</td>
<td>505(^e)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{2a}\)From Ref. 8, unless otherwise stated. \(^{2b}\)Ref. 23. \(^{2c}\)Ref. 16. \(^{2d}\)Ref. 26. \(^{2e}\)Stretching frequency for P–Te in \((\text{Ph}_3 \text{P})_2 \text{Te} \), this work. \(^{2f}\)Ref. 10. \(^{2g}\)Ref. 27. \(^{2h}\)Ref. 28.

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Generally organophosphorus chalcogenides can be represented by the following two resonance structures, the dipolar form (I) or as (II) in which there is $d_n - p_n$ bonding between the phosphorus atom and the chalcogen atom ($X = O, S, Se, and Te$).

\[
R_3P^+X^- \quad \quad \quad \quad R_3P=X
\]

(II)

Stretching frequencies of phosphorus chalcogenides are known to be a poor measure for the electronic distribution and hybridization in the $P-X$ bond. As pointed out by Goubeau, from an extensive study on the phosphorus-sulfur bond, differences in $P-S$ force constants in phosphorus sulfur compounds may be traced to several factors which have been demonstrated separately in different examples. The increase in calculated force constant for the $P-X$ bond in tris-dimethylamino phosphine chalcogenides from the sulfide to the telluride has suggested that the Siebert rule may not at all be valid when comparing the different chalcogenides. Furthermore, the view of the bonding between the phosphorus and the chalcogen atom arrived at from studies of stretching frequencies, may be at variance with results obtained from X-ray crystallographic studies. ESCA has likewise been shown to be a method of limited usefulness when examining the $P-O$, $P-S$, and $P-Se$ bonds. Recently, McFarlane and Rycroft have developed a heteronuclear triple resonance technique to obtain $77Se$ chemical shift in organophosphorus selenides, and this appears to be a valuable method for the investigation of the factors determining the charge distribution in such compounds. The amount of negative charge on selenium in phosphorus selenides appears to be dependent upon not only $p_n - d_n$ bonding between selenium and phosphorus and the electronegativity of the substituents, but also the ability of the $p$ orbitals of the substituents, such as in trimethyl selenophosphate, to compete with those of the selenium atom.

Due to their dipolar nature, most phosphorus chalcogenides act as powerful donors to a series of acceptors, the phosphorus selenides making their most stable adducts with soft Lewis acids, while the oxides generally make their most stable adducts with hard ones.

Rather few structure determinations of these adducts have been performed, but generally when the phosphorus chalcogenides are donors, the formed adducts may formally be regarded O(II), S(II), and Se(II) compounds, and as such they are bent. In the 2:3 adduct between triphenyl phosphine sulfide and iodine, the $P-S-I$ angle is $106^\circ$, in the bridged adduct between triphenyl phosphine selenide and mercuric chloride, the $P-Se-Hg$ angle is $98^\circ$. In tellurium bis(dimethylthiophosphophate), bis(diethylthiophosphoryl) diselenide, tellurium bis(diethylthioselenophosphinate), and selenium bis(diethyl-diselenophosphinate) the $P-X-M$ angles lie in the $103 - 106^\circ$ range.

The linear configuration of the $P-Te-P$ skeleton in the present adduct suggests that the phosphine telluride is not the donor, although a tervalent phosphorus compound may well behave as an acceptor. However, the total number of valency electrons in the $P-Te-P$ skeleton is 22. Walsh has given a correlation diagram for the orbitals of linear and non-linear triatomic molecules in their ground states. Using this diagram it is seen that the apex
angle reaches a minimum for molecules with 20 electrons, but that molecules with 22 electrons are linear. (The fact that other groups could contribute electrons to orbitals of a triatomic skeleton, as the phenyl groups are required to do in the above, was recognised by Walsh when he compared the ground states of allene and ketene with that of CO$_2$.) Thus, the linear structure of Ph$_3$PTePPh$_3$ is in accord with previous theoretical ideas, and accordingly is similar in structure to other systems containing 22 valence electrons such as the triiodide ion I$_3^-$ and, similarly, the tribromide ion, Br$_3^-$. No iso-electronic species from the fifth main group appear to have been synthesized. The bis(triphenylphosphine)iminium cation, ($\text{Ph}_3\text{P})_2\text{N}^+$, and the chlorite ion, ClO$_2^-$, both iso-electronic with tellurium(II) compounds, are angular, as are the examples of 20-electron systems originally listed by Walsh.

Whilst the above gives a satisfactory overall view of the bonding in the adduct, it is interesting to speculate in a little more detail on the changes in the orbitals which occur as the adduct is formed. Taking a naive view point, if tellurium acts as donor to phosphorus, the lone pair electrons on phosphorus are superfluous, or alternatively, if phosphorus acts as donor to tellurium, the lone pair on tellurium is. Whichever its origin, this pair of electrons may be compared with the pair discussed by Walsh in going from a 20- to a 22-electron system. Thus, if tellurium acts as donor, an angular system is observed with a stereochemically significant lone pair in an orbital localized on the central atom.

An alternative description of the formation of the bond between triphenyl phosphine and triphenyl phosphine telluride is analogous to the one suggested by Pimentel and Rundle for the formation of the triiodide ion, I$_3^-$, from iodide and iodide. In this description, the three-center four-electron bond system, the extra two electron pairs, one from each donor, are combined with the 5$p^2$ orbital of the central atom without employing outer d-orbitals.

With regard to the weak tellurium-phosphorus bond, this bond may be regarded as formed by an interaction between the lone pair of the phosphorus atom and the σ* orbital of the normal phosphorus-tellurium bond, what is termed a "secondary bond" by Alcock. Fundamentally, this "secondary bond" and the "normal" bond is the same as an unsymmetrical three-center four-electron system with a tellurium atom of zero charge as central atom.

It is not clear why the P–Te bond lengths should be dissimilar within a given molecule, nor why they should vary from one molecule to another within the unit cell (see Table 2). It seems likely that lattice effects and electrostatic effects may be exerting a significant influence on bond lengths in three-center four-electron bond systems, as has been shown for the triiodide ion.

A possible explanation for the non-existence of triphenyl phosphine telluride and the stability of the present adduct is to consider triphenyl phosphine telluride to be polarized in the following way in view of the low electronegativity of tellurium relative to phosphorus in triphenyl phosphine:

\[ \delta^- \quad \sigma^* \]

\[ \text{Ph}_3\text{P} \quad \text{Te} \]

This implies that triphenyl phosphine telluride is the acceptor in the interaction with triphenyl phosphine. When forming the adduct with triphenyl phos-

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phine, the electron demand of the tellurium atom will be satisfied by the electron pair of the incoming phosphine. In this connection it is worth noticing that phosphine tellurides with weakly electronegative substituents bonded to phosphorus are rather stable compounds and show no ability to form adducts with an extra tervalent phosphorus compound.\(^\text{13}\)

Undoubtedly the large polarizability of the tellurium atom and the drop, albeit slight, in electronegativity from selenium to tellurium, combined with the electronegative nature of the phenyl groups, should make the above-mentioned resonance structure possible in the case of the unstable triphenyl phosphine telluride.

The exceptional behaviour of organophosphorus tellurides appears to have been noted once in the literature. Trinuclear iron carbonyls containing tellurium were found to add tributyl phosphine without displacing one molecule of carbon monoxide, contrary to what was found for the similar sulfur and selenium compounds.\(^\text{46}\) No definite proof, however, was given for the suggested structure of the addition compound, or for the occurrence or involvement of organophosphorus tellurides.

**EXPERIMENTAL**

Tetraphenylarsaronium tellurocyanate, tetraphenylarsaronium cyanide, triphenyl phosphine, and acetonitrile were purified as reported.\(^\text{19}\) Lithium perchlorate (Fluka purum, Wasserfrei) and acetone, “Baker Analyzed” reagent, were used without further purification.

The adduct between triphenyl phosphine telluride and triphenyl phosphine: To 1 g tetraphenylarsaronium tellurocyanate, 1.86 mmol, dissolved in 20 ml purified acetonitrile, carefully flushed with dry nitrogen, was added 2 g triphenyl phosphine, 7.64 mmol. A slight increase of the yellow colour could be observed. A total amount of 0.34 g lithium perchlorate, 3.2 mmol, in 10 ml acetonitrile, was then added very slowly. After addition of the first drop of this solution, the colour changed immediately to cream yellow; the colour increased in intensity as more lithium perchlorate was added.

After half the lithium perchlorate had been added, a yellow crystalline compound started to separate. On further addition, tetraphenylarsaronium perchlorate and lithium isocyanide started to precipitate as well. After stirring for some minutes at room temperature, 2 g of triphenyl phosphine in 15 ml acetonitrile was added, making a total volume of 45 ml. The reaction mixture was then stirred at 35\(^\circ\)C until the white precipitates had dissolved. The yellow, microcrystalline product was filtered from the reaction mixture and dried. Yield 0.71 g, 59 %. Evaporation of the solvent in vacuum left more yellow crystals among the otherwise white products and reactants. No blackening due to deposed tellurium was observed during the evaporation. A manual separation of the yellow product from the white residue proved tedious and not satisfactory.

The adduct was dissolved in 20 ml acetone containing 3 g triphenylphosphine, traces of tellurium dioxide and elemental tellurium were filtered off, and the clear solution was left at 0\(^\circ\)C for a couple of hours until the first crystals of triphenyl phosphine appeared. The product was rapidly filtered, washed with some ice-cold acetone containing triphenyl phosphine, and dried. The final, overall yield of pure compound was never found to be higher than 30 %, as a considerable amount of the product was left in the mother liquor. The decomposition temperature of the adduct was 83 – 85\(^\circ\)C, slightly above that of the melting point of triphenyl phosphine, 80 – 81\(^\circ\)C. (Found: C 66.85; H 5.04; N negative: Calc. for C\(_{34}\)H\(_{30}\)P\(_{2}\)Te: C 66.25, H 4.65.)

The reaction between tetraphenylarsaronium tellurocyanate and triphenyl phosphine in the presence of lithium perchlorate was followed by measuring the peak height at 2081 cm\(^{-1}\) using IR liquid cells.\(^\text{19}\) The measurements were performed with a Unicam SP 200 G Infrared Spectrophotometer (see Table 1).

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The spectra (4000 - 250 cm⁻¹) were measured on KBr discs using a Perkin-Elmer 457 spectrophotometer; no blackening was observed in the disc and the peaks were in the same positions as in the less well-resolved nujol spectrum. From 400 - 40 cm⁻¹ the spectra were measured by the Physico-Chemical Measurements Unit at Harwell as pressed polythene discs. Raman spectra were recorded at the Nottingham University.

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REFERENCES


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