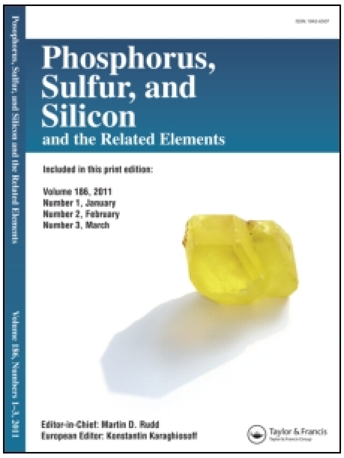


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS OF TRIPHENYLPHOSPHINE AND TRIBUTYLPHOSPHINE WITH TETRAETHYLTHIURAM DISULFIDE AND DIETHYLDITHIOCARBAMATE COMPLEXES OF TELLURIUM(II) AND TELLURIUM(IV)

R. Krishna Kumar[a]; G. Aravamudan[a]; M. R. Udupa[a]
[a] Department of Chemistry, Indian Institute of Technology, Madras, India

To cite this Article Kumar, R. Krishna , Aravamudan, G. and Udupa, M. R.(1996) 'REACTIONS OF TRIPHENYLPHOSPHINE AND TRIBUTYLPHOSPHINE WITH TETRAETHYLTHIURAM DISULFIDE AND DIETHYLDITHIOCARBAMATE COMPLEXES OF TELLURIUM(II) AND TELLURIUM(IV)', Phosphorus, Sulfur, and Silicon and the Related Elements, 114: 1, 39 — 49
To link to this Article: DOI: 10.1080/10426509608046409
URL: http://dx.doi.org/10.1080/10426509608046409

Phosphorus, Sulfur, and Silicon, 1996, Vol. 114, pp. 39–49
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIONS OF TRIPHENYLPHOSPHINE AND TRIBUTYLPHOSPHINE WITH TETRAETHYLTHIURAM DISULFIDE AND DIETHYLDITHIOCARBAMATE COMPLEXES OF TELLURIUM(II) AND TELLURIUM(IV)

R. KRISHNA KUMAR, G. ARAVAMUDAN† and M. R. UDUPA
Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

(Received November 15, 1995; in final form February 27, 1996)

Triphenylphosphine reduces tetrakis(diethyldithiocarbamato)tellurium(IV), TeL_4 [L = diethyldithiocarbamate, $(C_2H_5)_2NCS_2^-$] to the tellurium(II) complex TeL_2, on which PPh_3 has no effect. The reaction of the tellurium(IV) complex, TeL_2X_2 (X = I, Br, Cl) with PPh_3 in the molar ratio of 1:1 results in the formation of TeLX, CS_2 and an aminophosphonium halide, $(C_2H_5)_2N\overset{+}{P}Ph_3X^-$. Another mole of PPh_3 reduces TeLX further to elemental tellurium. The reactions of TeL_3X (X = I, ClO_4, PF_6) systems with excess PPh_3 lead interestingly to the formation of TeL_2 and elemental tellurium, with the concomitant formation of CS_2, $(C_2H_5)_2N\overset{+}{P}Ph_3X^-$ and $(C_2H_5)_2NC(S)\overset{+}{P}Ph_3X^-$. The reactions were performed in dichloromethane solutions and ^{31}P NMR spectroscopy was widely used for the identification of various phosphorus containing species.

Key words: Tellurium(II) and (IV) complexes, mixed halide-dithiocarbamate complexes, triphenylphosphine, tributylphosphine and ^{31}P NMR studies.

INTRODUCTION

The sulfur coordinated complexes of tellurium have received considerable attention owing to the interest in their stereochemistry and supramolecular activity.[1] During our continuing studies on mixed halide-dithiocarbamate complexes of tellurium(II) and (IV), we have synthesized and determined the structures of numerous complexes.[2–8] With diethyldithiocarbamate and iodide as ligands, all the three possible mixed halide-dithiocarbamate complexes of tellurium(IV), TeL_3I, TeL_2I_2 and $TeLI_3$ have been prepared.[2,3,9] All the three complexes have distorted pentagonal bipyramidal geometry around tellurium.[2–4] Thus these Te(IV) complexes prefer seven coordination in the solid state. While TeL_3I is monomeric in the solid state, TeL_2I_2 is a dimer and $TeLI_3$ is polymeric. It is of interest to mention here that TeL_2I_2 exists as a monomer in dichloromethane solution. The Te(II) complexes,[5,6] TeLX (X = Cl, Br, I) have halide bridged polymeric structures in the solid state, while in dichloromethane solution, TeLI exists as a dimer and TeLCl is monomeric. Thus, both Te(IV) and Te(II) complexes are coordinatively unsaturated in solution.

Reactions of various ligands with these complexes have been carried out. The addition of iodide to the complexes $TeLI_3$ and TeLI yielded novel adducts $[(C_2H_5)_4N][TeLI_4]$ and $[(C_2H_5)_4N][TeLI_2]$ respectively.[7,8] Apart from addition reac-

---

†Author to whom correspondence should be addressed.

tions, TeLX complexes undergo metathetical reactions with thiourea and substituted thioureas and disproportionation with 1,10-phenanthroline hydrate.[8]

In addition to being a π-acceptor ligand, triphenylphosphine is also a good reducing agent. In the reactions with various mixed halide-dithiocarbamate complexes of tellurium(II) and (IV), the triphenyl or tributylphosphines can either add to tellurium in a coordinatively unsaturated complex or reduce Te(II) or Te(IV) to elemental tellurium. This is the first detailed study of the reaction of triphenyl and tributylphosphine with mixed halide-diethyldithiocarbamate complexes of tellurium(II) and (IV). The ^{31}P NMR spectroscopy was a handy tool for these studies.

EXPERIMENTAL

The complexes TeL_4,[10] TeL_3X (X = I, ClO_4),[9,11] TeL_2X_2 (X = Cl, Br, I)[2] and TeLX (X = Cl, Br, I)[5,6] were prepared by previously reported procedures. The complex TeL_3PF_6 was obtained by addition of a methanol solution of KPF_6 to a dichloromethane solution of TeL_3ClO_4. The $KClO_4$ formed was removed by filtration. The brown colored filtrate in a dichloromethane-ethylacetate mixture yielded stubby needle like crystals. Triphenylphosphine was obtained from Aldrich and used without further purification.

The NMR spectra were recorded on a 400 MHz JEOL GSX-400 spectrometer. ^{31}P NMR spectra were measured in dichloromethane solution at 161.0 MHz and referenced against 85% H_3PO_4. The chemical shift values of the resonances were arrived at using high frequency positive convention. The various products obtained were thoroughly characterized by elemental analyses and X-ray diffraction studies.

RESULTS AND DISCUSSION

Reactions of Triphenylphosphine with Tellurium(II) Complexes

Triphenylphosphine does not react with TeL_2 in non-aqueous media as observed from the ^{31}P NMR, in which only the signals due to the unreacted PPh_3 is observed.

However, the dichlormethane solution of TeLI is immediately reduced to elemental tellurium by triphenylphosphine. Preliminary studies indicate that neither thiuram disulfide nor iodine is the oxidation product, suggesting that PPh_3 must have been oxidized. Thus to explore the reaction mechanism in detail ^{31}P NMR spectra of dichloromethane solutions of reactants in different mole proportions were measured and from the chemical shift values the course of the reaction has been followed. The ^{31}P chemical shifts observed and their corresponding assignments are listed in Table I.

In the reaction of TeLI with PPh_3, apart from elemental tellurium, a colorless dichloromethane soluble gummy residue (which failed to solidify under different experimental conditions) was obtained. But on exposure to air its color becomes red within a day, testing for iodine, which would have resulted due to aerial oxidation, thus suggesting that the product contains an iodide.

Further, it was observed that the reaction of PPh_3 with TeLX liberates carbon disulphide. The evolution of CS_2 is confirmed by the formation of the characteristic bis(2,2′-dihydroxyethyldithiocarbamato)nickel(II) complex when the evolved gas is allowed to react with a methanolic solution of nickel(II) chloride and diethanolamine.

The ^{31}P NMR spectrum (Figure 1a) of an equimolar mixture of TeLI and PPh_3 shows a signal at 29.9 ppm. Similarly, for the bromo and chloro analogues the resonance is observed at 27.7 and 26.8 ppm respectively (Figures 1b and 1c). An

TABLE I

^{31}P NMR data of Te-dtc-PPh_3 systems in CH_2Cl_2 at 25°C

System	^{31}P Chemical shifts (δ ppm)	Assignment
L-L+PPh_3	-6.8 26.5 41.8	PPh_3 $(C_2H_5)_2NCS_2\overset{+}{P}Ph_3L^-$ $SPPh_3$
TeL_4 + PPh_3	-5.9 27.2 42.7	PPh_3 $(C_2H_5)_2NCS_2\overset{+}{P}Ph_3L^-$ $SPPh_3$
TeL_2I_2 + PPh_3	-6.0 29.9	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3I^-$
TeLI + PPh_3	-6.0 29.9	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3I^-$
TeL_2Br_2 + PPh_3	-5.9 28.4	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3Br^-$
TeL_2Cl_2 + PPh_3	-6.0 26.4	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3Cl^-$
TeLBr + PPh_3	-6.8 27.7	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3Br^-$
TeLCl + PPh_3	-6.8 26.8	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3Cl^-$
TeL_3I + PPh_3	-6.8 28.0 41.8	PPh_3 $(C_2H_5)_2N\overset{+}{P}Ph_3I^-$ $SPPh_3$
TeL_3PF_6 + PPh_3	-145.5 (heptet) -6.8 18.3 27.3 41.9	PF_6^- PPh_3 $(C_2H_5)_2NCS\overset{+}{P}Ph_3PF_6^-$ $(C_2H_5)_2N\overset{+}{P}Ph_3PF_6^-$ $SPPh_3$
TeL_3ClO_4 + PPh_3	-6.9 18.3 26.7 41.9	PPh_3 $(C_2H_5)_2NC(S)\overset{+}{P}Ph_3ClO_4^-$ $(C_2H_5)_2N\overset{+}{P}Ph_3ClO_4^-$ $SPPh_3$
TeLI + $(n\text{-}Bu)_3P$	-13.9 18.8 48.4 56.0	$(n\text{-}Bu)_3PTe$ $(n\text{-}Bu)_3\overset{+}{P}C(S)S^-$ $(C_2H_5)_2N\overset{+}{P}(n\text{-}Bu)_3I^-$ $(n\text{-}Bu)_3PS$

internal redox reaction seems to occur initially with TeLX, to give elemental tellurium and the oxidized species, $[(C_2H_5)_2NCS_2]^+$, which can react further with PPh_3. The product that seems to form in this reaction is $(C_2H_5)_2N\overset{+}{P}Ph_3X^-$ (**1**), N,N-diethylaminotriphenylphosphonium halide and CS_2. It is known that the ^{31}P NMR chemical shifts are found[12–14] to occur in the region 25–50 ppm for the aminophosphonium compounds. Thus the resonance located around 28 ppm is reasonably assigned to the ion pair $(C_2H_5)_2N\overset{+}{P}Ph_3X^-$. The chemical shift values decrease as expected on going from iodide to chloride in the ion pairs. The elemental microanalysis for carbon, hydrogen and nitrogen and macroanalysis for the halide of the compound also conformed to the above formulation. The analogous N,N′-dimethylaminotriphenylphosphonium tribromide has been prepared and its crystal structure reported.[15]

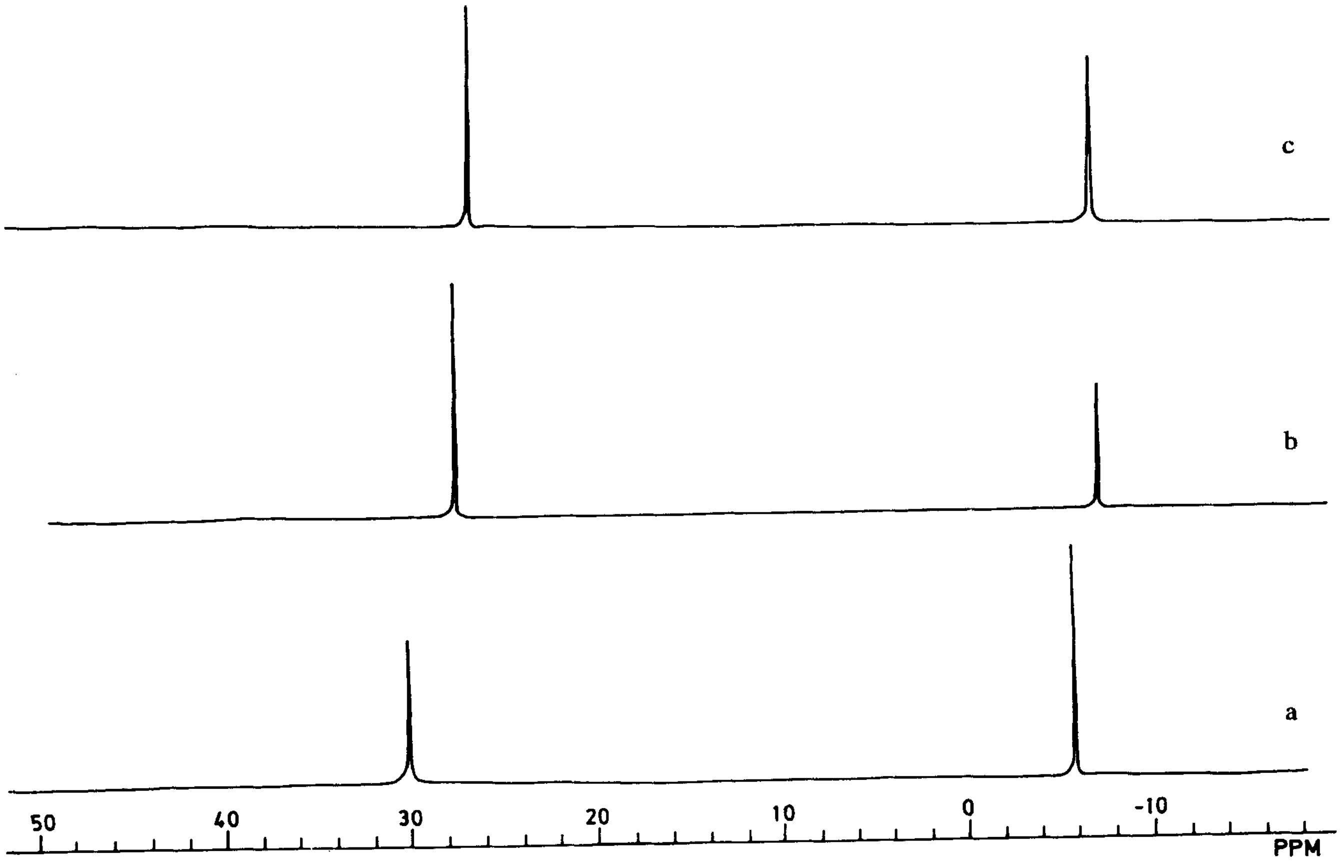


FIGURE 1 ^{31}P NMR measured in CH_2Cl_2 of a mixture of a) TeLI and PPh_3, b) TeLBr and PPh_3, and c) TeLCl and PPh_3 in 1:2 molar ratio.

Reactions of Triphenylphosphine with Tellurium(IV) Complexes

In the reaction with triphenylphosphine, TeL_4 gets reduced to TeL_2. The reaction can be explained as mainly due to the initial autoredox reaction of TeL_4,[16-20] giving rise to TeL_2 and tetraethylthiuram disulfide (L—L) followed by the oxidation of triphenylphosphine by disulfide to yield triphenylphosphine sulfide (Equation 1).

$$TeL_4 \rightleftharpoons TeL_2 + L{-}L \xrightarrow{PPh_3} LP^+Ph_3L^- \rightarrow SPPh_3 + (C_2H_5)_2NC(S)S(S)CN(C_2H_5)_2 \qquad (1)$$

The reaction of triphenylphosphine with thiuram disulfide has been studied earlier.[21] The ^{31}P NMR spectrum (Figure 2a) of a solution containing an equimolar mixture of L—L and PPh_3 in dichloromethane gives three resonances with δ values 41.8, 26.6 and −6.8 ppm, which are due to $SPPh_3$, $(C_2H_5)_2NC(S)S\overset{+}{P}Ph_3L^-$ (**2**) and unreacted PPh_3 respectively. In this reaction, PPh_3 cleaves the S—S bond of the disulfide to yield an intermediate, **2**, which gets converted slowly to the monosulfide, $(C_2H_5)_2NC(S)S(S)CN(C_2H_5)_2$ (**3**) and triphenylphosphine sulfide as shown in Equation 1. However, this reaction goes to completion immediately on addition of methanol.

The spectrum of the dichloromethane solution of TeL_4 and PPh_3 (Figure 2b) shows identical resonances to that of a mixture of L—L and PPh_3, which clearly shows that the reaction of PPh_3 is with thiuram disulfide formed from the autoredox reaction of TeL_4.

In the molar ratio of 1:1, the reaction of TeL_2I_2 with PPh_3 in dichloromethane produces a color change from deep red to brown and the subsequent crystallization yields TeLI as one of the products. The ^{31}P NMR spectrum of the solution exhibited a very weak resonance at 41.8 ppm due to $SPPh_3$ and a more intense resonance at 29.6 ppm, which is similar to that obtained for the reaction of TeLI with PPh_3. However, the dichloromethane solution of TeL_2I_2 with PPh_3 in the molar ratio of 1: 2 precipitates elemental tellurium almost instantaneously and the reaction mixture is colorless. The NMR spectrum of this solution also gives a resonance around 30 ppm. Similarly, the solutions of PPh_3 with TeL_2Br_2 and TeL_2Cl_2 in a molar ratio 2:1 also precipitates elemental tellurium and give predominant ^{31}P resonances around 28 ppm.

The first stage in the reaction of TeL_2I_2 with PPh_3 is the reduction of the Te(IV) complex to TeLI with the formation of $(C_2H_5)_2N\overset{+}{P}Ph_3I^-$ (Equation 2). In the second stage another mole of PPh_3 reduces TeLI further to elemental tellurium (Equation 3).

$$Te[S_2CN(C_2H_5)_2]_2X_2 + PPh_3 \rightarrow Te[S_2CN(C_2H_5)_2]X + CS_2 + (C_2H_5)_2N\overset{+}{P}Ph_3X^- \qquad (2)$$

$$Te[S_2CN(C_2H_5)_2]X + PPh_3 \rightarrow Te + CS_2 + (C_2H_5)_2N\overset{+}{P}Ph_3X^- \qquad (3)$$

In the TeL_3X system, TeL_3I, TeL_3ClO_4 and TeL_3PF_6 were chosen for the reaction with PPh_3, as ClO_4^- and PF_6^- have considerably different coordination abilities compared to iodide. It is interesting to note that the reaction of TeL_3X with PPh_3 differs markedly from those of TeL_2X_2 and TeLX with PPh_3.

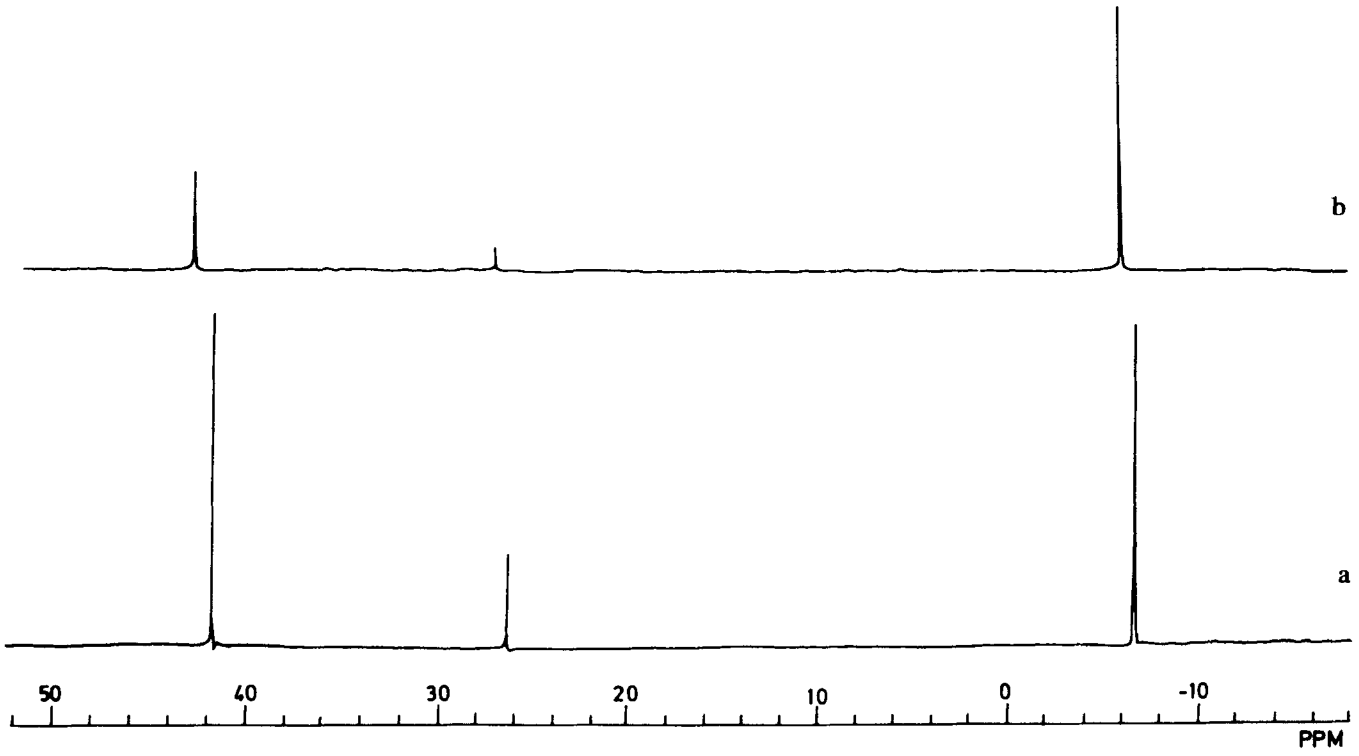


FIGURE 2 The ^{31}P NMR spectra of an equimolar mixture of a) thiuram disulfide and PPh_3 in 1:2 molar ratio, and b) TeL_4 and PPh_3 in 1:4 molar ratio.

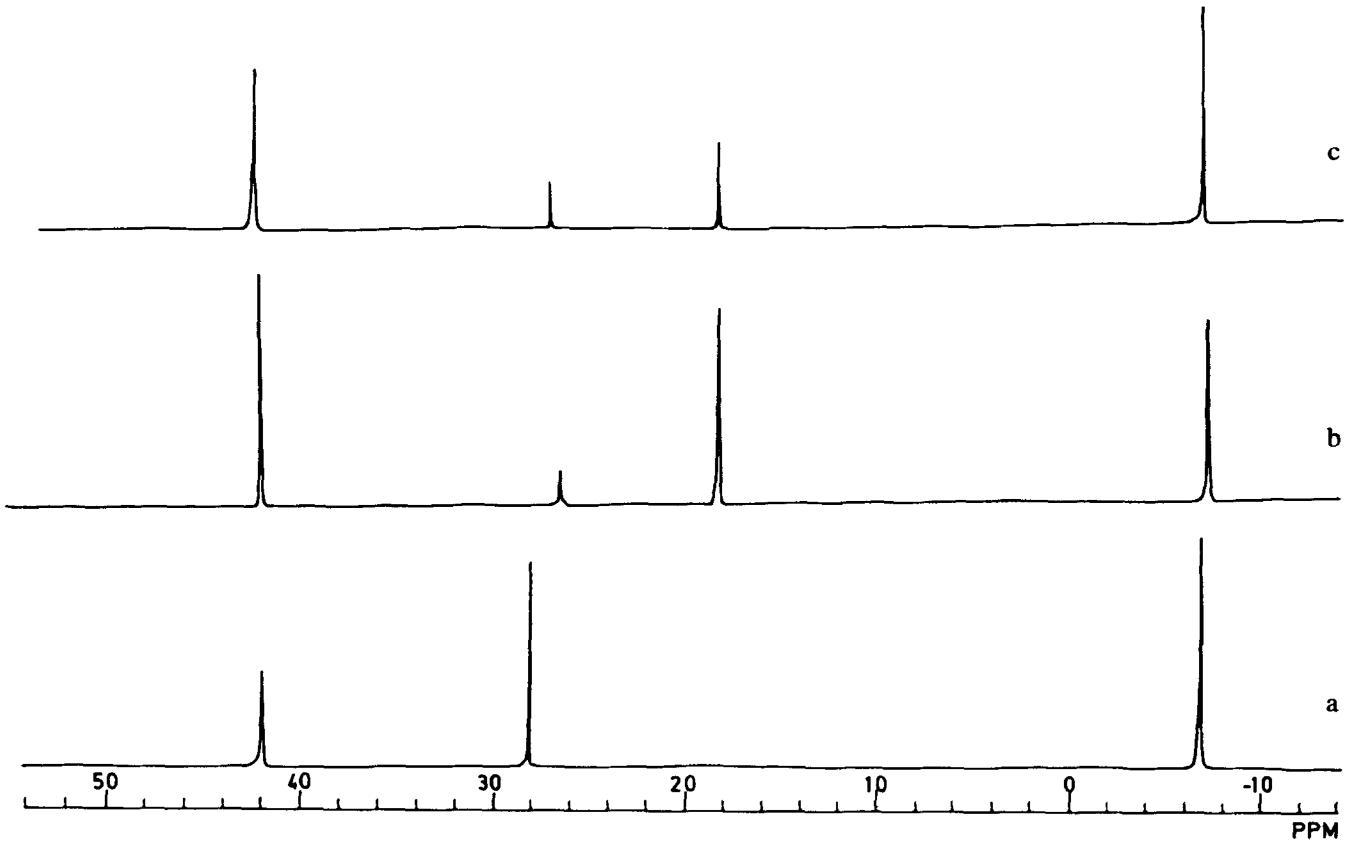
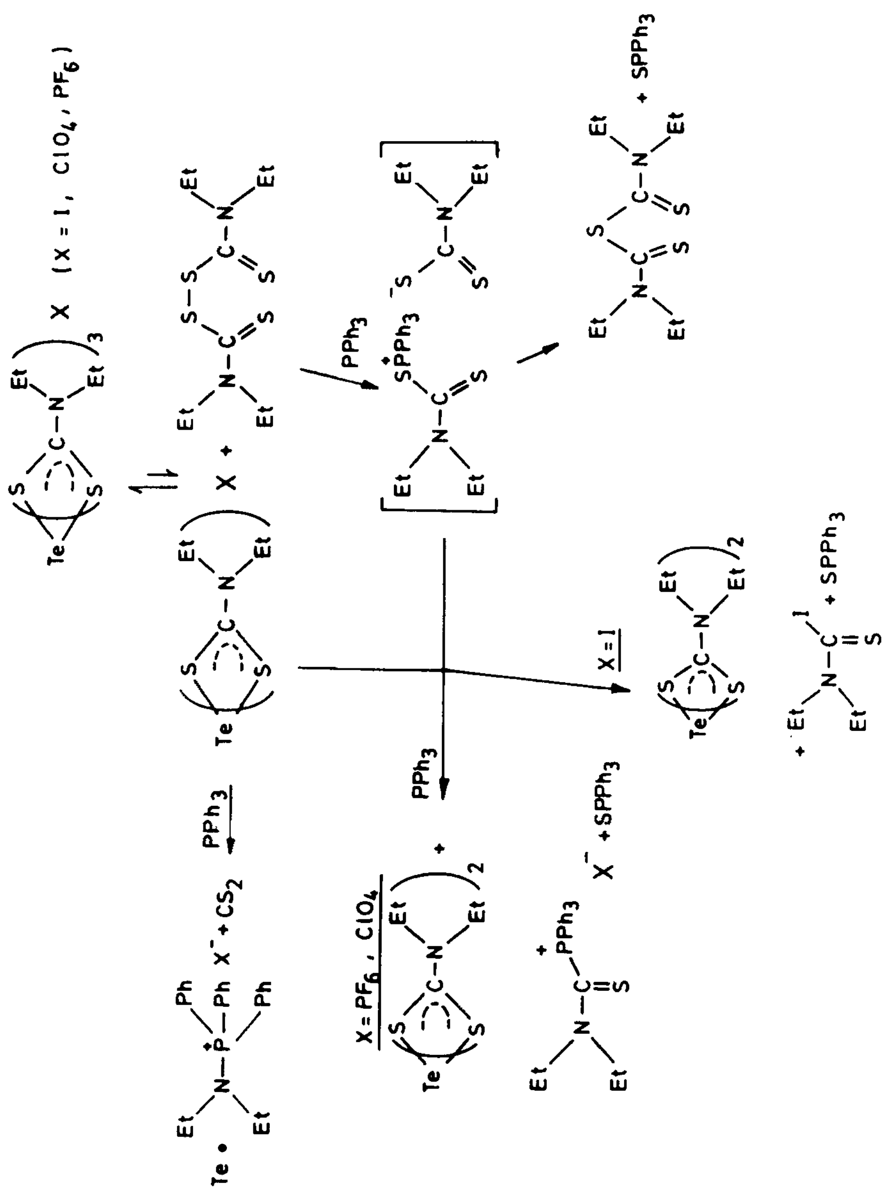


FIGURE 3 ^{31}P NMR measured in CH_2Cl_2 of a) TeL_3I and PPh_3, b) TeL_3ClO_4 and PPh_3, and c) TeL_3PF_6 and PPh_3 in 1:4 molar ratio.


X (X = I, ClO4, PF6)
Te
PPh3
Te + Et2N–P⁺Ph3 X⁻ + CS2
X = PF6, ClO4
X⁻ + SPPh3
X = I
+ SPPh3

SCHEME 1

The addition of PPh_3 to TeL_3I in the molar ratio of 4:1 in dichloromethane yielded only a small proportion of elemental tellurium and the solution remained red colored. Crystallization of the products show that TeL_2 and $SPPh_3$ are present. Similar observations were made in the case of TeL_3ClO_4 and TeL_3PF_6.

The ^{31}P NMR spectrum (Figure 3a) of the dichloromethane solution containing TeL_3I and PPh_3 in the molar ratio 1:4 has resonances at −6.8, 28.0 and 41.8 ppm, which are due to PPh_3, $(C_2H_5)_2N\overset{+}{P}Ph_3I^-$ and $SPPh_3$ respectively. However, the reaction mixture of TeL_3PF_6 and that of TeL_3ClO_4 with PPh_3 give almost identical ^{31}P NMR spectra, which apart from the resonances due to PPh_3, $SPPh_3$ and $(C_2H_5)_2N\overset{+}{P}Ph_3X^-$, contains a resonance around 18 ppm which is due to $(C_2H_5)_2NC(S)\overset{+}{P}Ph_3X^-$.[22]

In the reaction of the TeL_3X system with PPh_3, the first step of the reaction is the internal redox reaction, which is forced to occur in the presence of PPh_3 as shown in Scheme 1. The products obtained are TeLX and thiuram disulfide. Independent reactions (Equations 1 and 3) illustrate that the reaction of thiuram disulfide with PPh_3 yields an intermediate **2**, which slowly converts to $SPPh_3$ and **3**, and TeLX (X = I, Br, Cl) reacts with PPh_3 to yield elemental tellurium and aminophosphonium halide, **1**. The reaction of TeL_3X with PPh_3 differs from the reaction of TeL_2X_2 and TeLX with PPh_3 due to the presence of the disulfide in the system along with TeLX.

In the reaction of the disulfide with PPh_3, the conversion of **2** to **3** and $SPPh_3$, is a slow process, as evident from NMR experiments. Therefore, in TeL_3X complexes the final products are due to the competing reactions of TeLX, PPh_3, and **2**, as shown in Scheme 1.

In the reaction of TeL_3I and PPh_3, apart from the reaction of disulfide and TeLI with PPh_3, the prominant reaction seems to be that of the dithiocarbamate of **2** and TeLI to yield TeL_2. The nucleophile attack of displaced iodide on the thiocarbamyl carbon of the phosphonium cation results in the formation of $SPPh_3$, and thiocarbamyl iodide. As seen from the NMR spectrum, $SSPh_3$ is the major product obtained in this reaction and the conversion of TeL_3I to elemental tellurium and **1** occurs probably to a limited extent.

However, due to the poor nucleophilicity of ClO_4^- and PF_6^-, they cannot substitute for triphenylphosphine sulfide in **2**. Instead, PPh_3 itself displaces $SPPh_3$ giving rise to $(C_2H_5)_2NC(S)\overset{+}{P}Ph_3X^-$. The driving force for this reaction is the formation of TeL_2 and $SPPh_3$.

Reaction of Tri-n-Butylphosphine with TeLI

As shown in Equation 3, TeLI reacts with PPh_3 to give elemental tellurium, CS_2 and **1**. Tri-*n*-butylphosphine is known to react with elemental tellurium to give the phosphine telluride, which has a ^{31}P NMR resonance at −17.7 ppm,[23] and with carbon disulfide to yield the zwitter ion,[24] $(n\text{-}Bu)_3\overset{+}{P}C(S)S^-$, the resonance of which is observed at 18 ppm. Hence, in order to confirm the evolution of CS_2 in the reaction of TeLI with PPh_3, the reaction of TeLI with $(n\text{-}Bu)_3P$ was carried out.

The ^{31}P NMR (Figure 4) of the dichloromethane solution containing the reaction mixture of TeLI with $(n\text{-}Bu)_3P$ in a 1:3 molar ratio shows resonances at −13.9 ppm due to $(n\text{-}Bu)_3PTe$ and at 18.8 ppm due to $(n\text{-}Bu)_3\overset{+}{P}C(S)S^-$. In addition, signals at 48.4 and 56.0 ppm, of very low intensity appears due to $(n\text{-}Bu)_3\overset{+}{P}N(C_2H_5)_2I^-$ and (*n*-

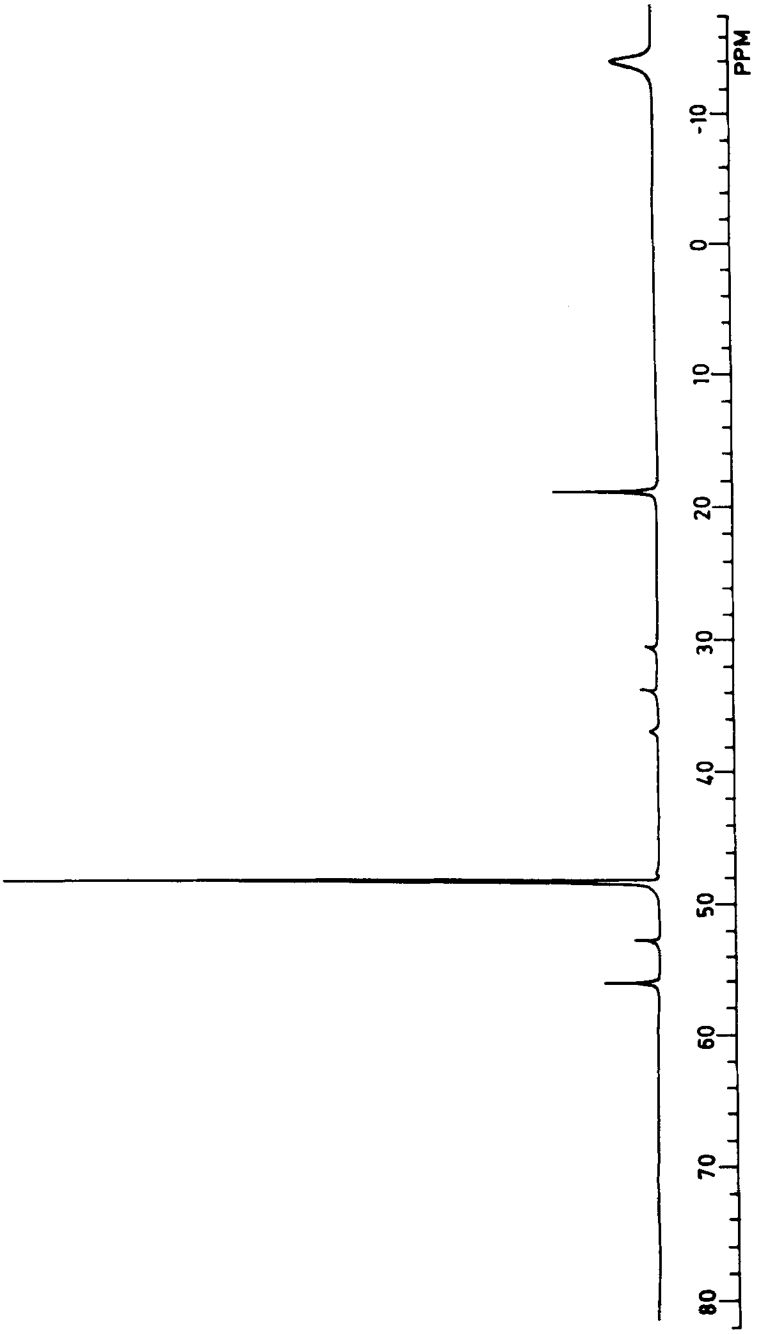


FIGURE 4 ^{31}P NMR spectra of a mixture of TeLI and (*n*-Bu)$_3$P in 1:3 molar ratio.

Bu)$_3$PS respectively. The resonances of free (n-Bu)$_3$P occurs at −32.6 ppm and the broad signal at −13.9 ppm is indicative of the exchange of free tributylphosphine with tributylphosphine telluride.

$$\mathrm{TeLI} + 3(n\text{-Bu})_3\mathrm{P} \rightarrow (n\text{-Bu})_3\mathrm{PTe} + (n\text{-Bu})_3\overset{+}{\mathrm{P}}(\mathrm{S})\mathrm{S}^- + (n\text{-Bu})_3\overset{+}{\mathrm{P}}\mathrm{N}(\mathrm{C_2H_5})_2\mathrm{I}^- \quad (4)$$

CONCLUSION

Triphenylphosphine does not react with bis(diethyldithiocarbamoto)tellurium(II). However, mixed halide-dithiocarbamate tellurium(II) complexes are reduced to elemental tellurium by triphenylphosphine. Tetrakis(diethyldithiocarbamato)tellurium(IV) is converted to bis(diethyldithiocarbamato)tellurium(II) by PPh$_3$. However, TeL$_3$X and TeL$_2$X$_2$ are reduced to either Te(II) or elemental tellurium depending on the reaction conditions. The reaction PPh$_3$ moiety forms the species SPPh$_3$, $(\mathrm{C_2H_5})_2\mathrm{N}\overset{+}{\mathrm{P}}\mathrm{Ph_3X^-}$ and $(\mathrm{C_2H_5})_2\mathrm{NC(S)}\overset{+}{\mathrm{P}}\mathrm{Ph_3X^-}$. In the reaction of TeLI with tributylphosphine, apart from the aminophosphonium halide and tributylphosphine sulfide, tributylphosphine telluride and the zwitter ion, $(n\text{-Bu})_3\overset{+}{\mathrm{P}}\mathrm{C(S)S^-}$ also formed.

REFERENCES

1. I. Haiduc, R. B. King and M. G. Newton, *Chem. Rev.*, **94,** 301 (1994).
2. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee and T. A. Hamor, *Acta Cryst., C,* **49,** 1328 (1993).
3. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee, P. Selvam and K. Yvon, *Polyhedron,* in press.
4. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee, P. Selvam and K. Yvon, submitted for publication.
5. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee and T. A. Hamor, *Polyhedron,* **12,** 2201 (1993).
6. R. Krishna Kumar, G. Aravamudan, M. R. Udupa and M. Seshasayee, *Polyhedron,* in press.
7. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee and K. Sivakumar, submitted for publication.
8. R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee and T. A. Hamor, submitted for publication.
9. S. P. Chidambaram, G. Aravamudan, M. Seshasayee, M. R. Snow and E. R. T. Tiekink, *Aust. J. Chem.*, **42,** 969 (1989).
10. G. St. Nikolov, N. Jordanov and I. Havezov, *J. Inorg. Nucl. Chem.*, **33,** 1055 (1971).
11. S. P. Chidhambaram, G. Aravamudan, M. Seshasayee, T. A. Shibanova and V. I. Simonov, *Polyhedron,* **7,** 1267 (1988).
12. L. K. Krannich, R. K. Kanjulia and C. L. Watkins, *Magn. Reson. Chem.*, **25,** 320 (1987).
13. S. R. Jain, W. S. Brey and H. R. Sisler, *Inorg. Chem.*, **6,** 515 (1967).
14. L. K. Krannich, R. K. Kanojolia and C. L. Watkins, *Inorg. Chim. Acta.*, **103,** 1 (1985).
15. L. Chiche and H. Christol, *J. Chem. Soc. Perkin Trans. II,* **753** (1984).
16. S. Husebye and S. E. Svaeren, *Acta Chem. Scand.*, **27,** 763 (1973).
17. W. Mazurek, *Inorg. Chim. Acta.*, **160,** 11 (1989).
18. A. M. Bond, S. Dakternieks, R. D. Giacomo and A. Hollenkamp, *Inorg. Chem.*, **28,** 1510 (1989).
19. W. Mazurek and A. G. Moritz, *Inorg. Chim. Acta.*, **154,** 71 (1988).
20. A. M. Bond, D. Dakternieks, R. D. Giacomo and A. F. Hollenkamp, *Organometallics,* **10,** 3310 (1991).
21. G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Pub. Co., 1962.
22. J. A. McCleverty and J. Morrison, *J. Chem. Soc., Dalton Trans.*, 541 (1976).
23. N. Kuhn, G. Henkel, H. Schumann and R. Frohlich, *Z. Naturforsch,* **45b,** 1010 (1990).
24. J. Emsley and D. Hall, "The Chemistry of Phosphorus," Harper and Row Pub., 1976, p. 133.