Oxidative Coupling of Tellurophosphoranes, a Route to Phosphane Stabilised Tritellurium Dications

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Tellurophosphoranes $R_3P{=}Te$ (**1**) are oxidised by ferricenium salts to give the dications $R_3P{-}Te{-}Te{-}Te{-}PR_3^{2+}$ (**2**); the crystal structure of (**2**; R = Bu^t) has been obtained.

The ylidic nature of the phosphorus–tellurium double bond in trialkyl tellurophosphoranes (**1**) has been demonstrated by their ligand properties recently.[1,2] The low bond order of 1.5 in $Bu^t_3P{=}Te$ (**1b**) (P–Te 2.368 Å),[3] which has also been found in amino substituted tellurophosphoranes,[4] is presumably a consequence of both the atomic radii and the small differences in the electronegativities of Te and P, and confirms a polar bond with high electron density at the tellurium atom. Phosphorus ylides are known to give $R_3P{-}CH_2CH_2{-}PR_3^{2+}$ dications on treatment with $CuCl_2$[5] and, similarly, oxidation of the ylidic selenide $(R_3P)_2CSe$ forms a Se–Se single bond.[6] Thus, oxidative coupling of tellurolates, which is a convenient method to prepare ditellurides,[7] should be parallelled by the oxidation of tellurophosphoranes.

In fact, tellurophosphoranes (**1**, R = Pr^i, Bu^t) react with ferricenium salts $[(C_5H_5)_2Fe]X$ ($X = BF_4, PF_6, SbF_6$) to give ionic tellurium products and ferrocene.† Surprisingly, from the reaction mixture, compounds of the type (**2**) could be isolated in moderate yields instead of the ditellurium dications (**3**) expected. The formation of the Te_3 unit is a step in the direction of the cluster formation typical of tellurium chemistry as indicated by the stability of the cluster cations Te_4^{2+} and Te_6^{4+},[8] and electrical charge distribution may stabilise (**2**) relative to (**3**). For the same reason, coupling of thiophosphoranes gives stable cations $R_3P{-}S{-}S{-}PR_3^{2+}$ but only with dialkylamino substitutents.[9]

The dications (**2**) may be considered as tellurophosphorane Te^{2+} complexes (**4**) or, alternatively, as phosphane stabilised Te_3 dications (**5**). To gain insight into the properties of the PTe_3P unit we have undertaken an *X*-ray analysis of (**2b**) (Figure 1).‡

The Te–Te bond length of 2.71 Å is between the single bond distance calculated from covalent radii[10] of the element[11] (2.835 Å) and the double bond of the Te=Te molecule in the vapour phase[12] (2.61 Å), which is lengthened by side-on co-ordination.[13] The 'normal' single bond in organic ditellurides[14] of *ca.* 2.70 Å is suggested to be influenced by π-bonding which can be seen by its lengthening up to *ca.* 2.79 Å on co-ordination.[15] Thus, π-bonding should influence the Te_3 unit in (**2**) also.

$R_3P{=}Te$

(**1**)

a; R = Pr^i

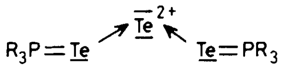
b; R = Bu^t

$[R_3P{-}Te{-}Te{-}Te{-}PR_3]^{2+}$

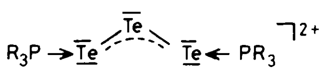
(**2**)

$[R_3P{-}Te{-}Te{-}PR_3]^{2+}$

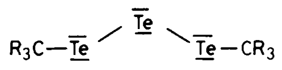
(**3**)



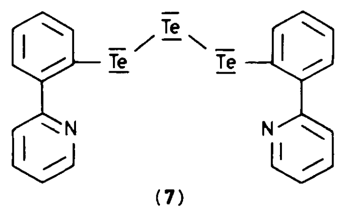
(**4**)



(**5**)



(**6**)



(**7**)

R = SiMe$_3$

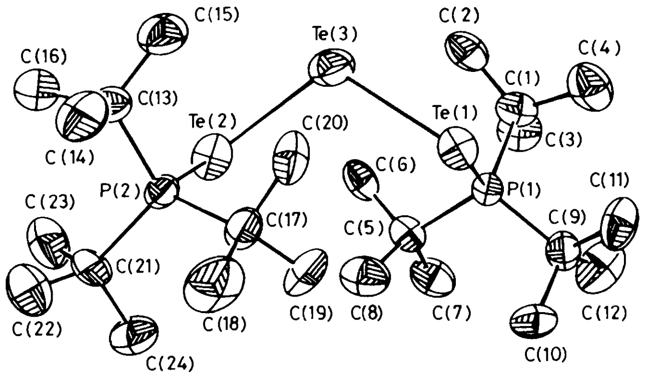


Figure 1. The structure of $[Bu^t_3PTe_3PBu^t_3]^{2+}$ (**2b**), SbF_6 salt. Selected bond lengths (Å) and angles (°): Te(1)–Te(3) 2.713(1), Te(2)–Te(3) 2.715(2), Te(1)–P(1) 2.492(3), Te(2)–P(2) 2.505(4), Te(1)–Te(3)–Te(2) 109.0(1), Te(3)–Te(1)–P(1) 108.4(1), Te(3)–Te(2)–P(2) 108.8(1). The Te(1) · · · Te(2) distance of 4.419 Å is in the range of the sum of the van der Waals radii. The interionic distances show no interaction.

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† Stoicheiometric amounts of ferricenium salt are added to (**1**) (2 g) in CH_2Cl_2 (20 ml) at −40 °C. After 30 min stirring, the product precipitates on addition of Et_2O (40 ml) as red-brown crystals (**2**), *ca.* 30% yield. All handling was carried out in the dark. N.m.r. spectra in CD_2Cl_2 at −40 °C: (**2a**) ^1H N.m.r. δ 1.44 [dd, Me, *J*(HH) 11.3, *J*(PH) 17 Hz], 2.80 (m, CH); ^{13}C n.m.r. δ 18.94 [d, Me, *J*(PC) 3 Hz], 26.19 [d, CH, *J*(PC) 23.9 Hz]; ^{31}P n.m.r. δ 49.7 p.p.m.; (**2b**) ^1H n.m.r. 1.78 [d, *J*(PH) 16.3 Hz]; ^{13}C n.m.r. 29.96 (s, Me), 46.02 [d, quat. C, *J*(PC) 6.5 Hz]; ^{31}P n.m.r. δ 79.4 p.p.m. No ^{125}Te n.m.r. data could be obtained owing to rapid decomposition.

‡ *Crystal data* for $[R_3PTe_3PR_3][SbF_6]_2$ (**2b**, R = Bu^t): triclinic, space group $P\bar{1}$, $a = 12.812(5)$, $b = 12.851(4)$, $c = 13.558(4)$ Å, $\alpha = 97.75(3)$, $\beta = 109.16(3)$, $\gamma = 97.00(3)°$; $U = 2056(1)$ Å^3, $Z = 2$, $D_c = 1.464$ g cm^{-3}, $\mu = 36.2$ cm^{-1}. The structure analysis is based on 5360 independent reflections (Mo-K_α, 2 $\theta_{max.}$ 50°), 4599 observed [$F_o \geqslant 3.5\sigma(F)$], empirical absorption correction (min./max. transmission 0.348/0.794). The structure was solved using Patterson methods and refined using SHELXTL to $R = 0.060$, $R_w = 0.068$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

However, the P–Te bond length of 2.50 Å indicates a weak single bond which is even longer than that observed in $Bu^t_3PTe{\cdot}W(CO)_5$[1] and $(R_2P)_2Te{\cdot}Cr(CO)_4$.[16] Therefore (**2**) should be considered as a phosphane complexed Te_3 dication (**5**) rather than a tellurophosphorane co-ordinated Te^{2+} ion (**4**). This result parallels our investigations on tellurophosphorane–iron complexes where Te–Fe π-bonding is discussed.[2] As a consequence of the weak P–Te bond, phosphanes are obtained as decomposition products of (**2**) in solution, no tellurophosphoranes being detected.

The Te_3 unit is also represented by the Te_3^{2-} ion[17] and the diorganyl tritellurides (**6**)[18] and (**7**).[19] The Te_3^{2-} ion and organotritelluride (**6**) have Te–Te bond lengths similar to that in (**2b**), while the lengthening in (**7**) (2.776 Å) may be interpreted as a consequence of secondary N–Te bonding. The reason for the differences in the Te–Te–Te angle [109.0° in (**2b**)] in the range of 100—110° is not clear.

Thus, the title cations (**2**) are unusual examples of tritellurium compounds and complete the tritelluride family.

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References

1 N. Kuhn, H. Schumann, and G. Wolmershäuser, *J. Chem. Soc., Chem. Commun.*, 1985, 1595.

2 N. Kuhn and H. Schumann, *J. Chem. Soc., Dalton Trans.*, 1987, 541.

3 N. Kuhn, H. Schumann, and G. Wolmershäuser, *Z. Naturforsch., Teil B*, 1987, **42**, 647.

4 S. Pohl, *Z. Naturforsch., Teil B*, 1978, **33**, 610; 1979, **34**, 256; C. Rømming, A. J. Iversen, and J. Songstad, *Acta Chim. Scand., Ser. A*, 1980, **34**, 333.

5 H. Schmidbaur, G. A. Bowmaker, U. Deschler, C. Doerzbacher, R. Herr, B. Milewski-Mahrla, A. Schier, and C. E. Zybill, *Phosphorus Sulfur*, 1983, **18**, 157; G. A. Bowmaker, C. Doerzbach, and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1984, **39**, 618.

6 H. Schmidbaur, C. E. Zybill, and D. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 156; *Angew. Chem. Suppl.*, 1983, 169.

7 'The Chemistry of Organic Selenium and Tellurium Compounds,' ed. S. Patai, Wiley Interscience, New York, 1986.

8 Gmelin Handbook of Inorganic Chemistry, Tellurium, Suppl. Vol. A2, Springer Verlag, Berlin, 1983.

9 W. E. Slinkard and D. W. Meek, *Chem. Commun.*, 1969, 361; *Inorg. Chem.*, 1969, **8**, 1811; E. W. Ainscough, A. M. Brodie, and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1980, 1042.

10 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, 1960.

11 P. Cherin and P. Unger, *Acta Crystallogr.*, 1967, **23**, 670.

12 A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon, Oxford, 1975.

13 O. Schneidsteger, G. Huttner, K. Dehnicke, and J. Pebler, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 428.

14 G. Llabres, O. Dideberg, and L. Dupont, *Acta Crystallogr., Sect. B*, 1972, **28**, 2438; S. Ludlow and A. E. McCarthy, *J. Organomet. Chem.*, 1981, **219**, 169; D. J. Sandman, J. C. Stark, and B. M. Foxman, *Organometallics*, 1982, **1**, 739; R. A. Zingaro, C. Herrera, and E. A. Meyers, *J. Organomet. Chem.*, 1986, **306**, C36.

15 F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rogers, J. M. Cummings, and I. Bernal, *J. Chem. Soc., Dalton Trans.*, 1981, 1004; J. L. Atwood, I. Bernal, F. Calderazzo, L. G. Canada, R. Poli, R. D. Rogers, C. A. Veracini, and D. Vitali, *Inorg. Chem.*, 1983, **22**, 1797.

16 R. Hensel, W. W. du Mont, R. Boese, D. Wewers, and L. Weber, *Chem. Ber.*, 1985, **118**, 1580.

17 A. Cisar and J. D. Corbett, *Inorg. Chem.*, 1977, **16**, 632.

18 F. Sladky, B. Bildstein, C. Rieker, A. Gieren, H. Betz, and T. Hübner, *J. Chem. Soc., Chem. Commun.*, 1985, 1800.

19 T. A. Hamor, N. Al-Salim, A. A. West, and W. R. McWhinnie, *J. Organomet. Chem.*, 1986, **310**, C5.