Organophosphorus-Tellurium Chemistry: From Fundamentals to Applications

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1. INTRODUCTION

Compounds incorporating phosphorus-chalcogen (P–E; E = S, Se) bonds are versatile reagents in both organic and inorganic synthesis. The best known example Lawesson's reagent [(4-MeOC₆H₄)P=S(μ-S)]₂ is widely used in organic chemistry, *e.g.* for the conversion of C=O to C=S groups.¹⁻⁴ More recently a selenium analog [PhP=Se(μ-Se)]₂, known as Woollins' reagent, has been shown to have wide applications in a variety of transformations.^{5,6} In addition, organophosphorus-chalcogen compounds are used as pesticides or nerve agents, as precursors for metal chalcogenide thin films or nanoparticles, in metal extraction processes and as lubricant additives. The chemistry of phosphorus-chalcogen compounds has been covered comprehensively in a recent book chapter that deals primarily with sulfur and selenium-containing systems.⁸

The behavior of organophosphorus-tellurium compounds is markedly different from that of the lighter chalcogen analogs, primarily as a result of the relative weakness of the P–Te bond. However, this characteristic can be employed advantageously in a variety of important transformations (*vide infra*). The first organophosphorus-tellurium derivative was described in 1950 by Foss, who observed that the treatment of potassium diethylphosphite with finely divided tellurium in warm ethanol produced the corresponding tellurophosphate K[(EtO)₂P(Te)O] as colorless, hygroscopic crystals that darkened rapidly in moist air.⁹ This area of phosphorus-chalcogen chemistry was stimulated by the discovery of the first tertiary phosphine telluride ⁿBu₃PTe in the early 1960s by Zingaro (Section 6.1).^{10, 11} Over the past 50 years this class of organophosphorus(V)-tellurium compound has attracted increasing attention, most notably as a source of reactive Te⁰ in the generation of semiconducting metal tellurides in the form of nanomaterials or quantum dots for applications as optoelectronic or thermoelectric materials and as infrared detectors or biomarkers (Section 6.7). Although neutral binary P–Te compounds are unknown, the recent characterization of the anion P₄Te₂²⁻ in solution¹² and, earlier, in a solid-state material¹³ may presage an extensive series of P–Te anions (Section 3). The challenge of

characterizing organophosphorus(III)-tellurium heterocycles in the solid state has recently been surmounted by using bulky substituents on phosphorus thus providing the opportunity to compare the ligand properties of organophosphorus-tellurium rings with the established behavior of their acyclic and lighter chalcogen analogs (Section 5.2).¹⁴

The driving force for much of the current interest in P–Te compounds is provided by the applications of a wide variety of metal tellurides as semi-conducting thin films or nanoparticles in solar cells, thermoelectric devices and IR detectors. Consequently, considerable attention is focused on the design of molecular precursors that will produce metal tellurides of high purity in the form of thin films or quantum dots. In this connection the weakness of the P–Te bond is an advantage and anionic ligands such as telluroimidophosphinates $[\text{R}_2\text{P}(\text{Te})\text{NR}']^-$ and ditelluroimidodiphosphinates $[\text{N}(\text{PR}_2\text{Te})_2]^-$ have proved to be suitable for these applications (Sections 7.3 and 8).^{15, 16} Other areas of current interest include the stabilization of electrophilic tellurium cations, e.g. Te^{2+} and ArTe^+ , by phosphine donors (Section 4)¹⁷ and weak $\text{P}^{\text{III}}\cdots\text{Te}$ interactions (Section 5.3).^{18, 19} The goal of this review is to provide a comprehensive account of organophosphorus-tellurium chemistry, including the historical development. It begins with a brief account of the strategies involved in investigations of phosphorus-tellurium chemistry. Subsequently, the discussion of each sub-topic will progress from a consideration of the rudiments for each class of phosphorus-tellurium compounds to a more advanced discourse culminating, where appropriate, in examples of applications, e.g. in organic chemistry and materials science. Comparisons will be made with the chemistry of the lighter chalcogen (S and Se) analogs, notably by using examples for which organophosphorus-tellurium compounds exhibit unique behavior. The literature is covered up to mid-2015.

2. FUNDAMENTAL CONSIDERATIONS

The synthesis of organophosphorus-tellurium compounds presents a number of challenges owing primarily to the relatively low thermal and photochemical stability of many derivatives.

Consequently, the preparation of compounds incorporating P–Te bonds should usually be carried out at low temperatures and, in certain cases, with protection from light. According to DFT calculations for the phosphine chalcogenides Me₃PE, this lability can be attributed, in part, to the marked decrease in the phosphorus-chalcogen bond energies down the series P–S (337) > P–Se (266) > P–Te (184) (in kJ mol^{–1}); however, multiple bonding becomes more important than the single bond for the heavier chalcogens.²⁰ A similar trend in P–E bond strengths for ⁿBu₃PE has been estimated on the basis of experimentally determined enthalpies of the reactions of ⁿBu₃P with chalcogens: P–S (401) > P–Se (314) > P–Te (218) (in kJ mol^{–1}).²¹ According to Hoff et al., these data suggest that simple dissociation of ⁿBu₃PTe to ⁿBu₃P and a Te atom should occur at a negligible rate and that the reactivity of ⁿBu₃PTe may result from an associative (intermolecular) process.²¹ For further discussion of the P–Te exchange process, see Section 6.2.

NMR spectroscopy is a powerful technique for monitoring the reactions of organophosphorus-tellurium compounds in solution. ³¹P NMR spectra ³¹P (*I* = ½, 100 %) are readily acquired and especially informative, e.g. in distinguishing between P^{III} and P^V centers on the basis of chemical shifts. In addition, the presence of the spin-active nuclei ¹²⁵Te (*I* = ½; 7.0 %) and ¹²³Te (0.9 %, *I* = ½) gives rise to satellites as a result of ³¹P–¹²⁵Te and ³¹P–¹²³Te coupling. The large variation of the one-bond spin-spin coupling constant ¹*J*(³¹P, ¹²⁵Te), which falls within the range of ca. 100 Hz to > 2,100 Hz, is primarily determined by the formal oxidation state of the phosphorus center (*vide infra*). ¹²⁵Te NMR spectra are more difficult to acquire, especially for poorly soluble compounds, but may provide a decisive indication of the environment of the tellurium centers based on the simple multiplet patterns resulting from coupling to one (doublet) or two (triplet) phosphorus centers. ¹²⁵Te NMR chemical shifts of organophosphorus-tellurium compounds embrace a very wide range of values in the range of ca. –1,000 to +1,000 (for a more detailed discussion, see Sections 5 and 6, Tables 1, 2 and 3). In some compounds that incorporate multiple phosphorus sites,

structural inferences can be made based on an analysis of the spin system for the most abundant isotopomers (see, for examples, Sections 3 and 5.2)

In addition to multinuclear NMR spectroscopic studies, much of the recent progress in organophosphorus-tellurium chemistry can be attributed to the acquisition of X-ray structures of thermally labile compounds. The sum of the covalent radii of phosphorus and tellurium is ca. 2.47 Å for a single bond and ca. 2.30 Å for a hypothetical double bond;²²⁻²⁴ the sum of the van der Waals radii is estimated to be 3.86 Å,²⁶ 4.12 Å²⁶ or 4.40 Å.²⁷ A close inspection of the available data indicates that the correlation between the values of $d(\text{P}-\text{Te})$ and $^1J(^{31}\text{P}, ^{125}\text{Te})$, if it exists, is limited to a narrow range of constitutionally and structurally similar compounds. The Fermi Contact (FC) term is only one of the three nucleus-electron interactions that contribute to the magnitude of the coupling constant between heavy nuclei, and all three depend on the gyromagnetic ratios. Consequently, the use of the reduced coupling constant, K_{PTe} , might be more appropriate.²⁸ The gyromagnetic ratio γ has a negative value for ^{125}Te , so ^{31}P - ^{125}Te couplings are negative. In practice, however, with a few exceptions (Section 3), the parameter $^1J(^{31}\text{P}, ^{125}\text{Te})$ is reported as an absolute value (magnitude only, without sign) in the literature and we have adopted that practice in this review. It is noted, however, that the frequently invoked correlation of trends in $^1J(^{31}\text{P}, ^{125}\text{Te})$ values with changes in the s (or p) character of the P–Te hybrid orbital must be regarded as an oversimplification, since the FC interaction is only one of the factors that determine the magnitude of $^1J(^{31}\text{P}, ^{125}\text{Te})$ in covalent organophosphorus-tellurium compounds. The elucidation of the relative contributions of these factors awaits a modern theoretical treatment (Section 5.3).

The two major classes of phosphorus-tellurium compounds based on the most common formal oxidation states of +3 or +5 are (a) acyclic and cyclic organophosphorus(III) compounds that incorporate a P–Te single bond and (b) organophosphorus(V) tellurides with terminal P=Te bonds (i.e. a formal double bond). The chemistry of these two categories is discussed in detail in Sections 5 and 6, respectively, but a consideration of their characteristic features is appropriate here.

Organophosphorus(V) tellurides typically exhibit P–Te bond lengths in the range 2.35–2.40 Å, which are affiliated with large $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling constants of 1650–2290 Hz. The highest values (> 2000 Hz) are observed for the amino-substituted phosphorus(V) tellurides $(\text{R}_2\text{N})_3\text{PTe}$ (e.g. R = Me, Et; R_2N = morpholino).²⁹ However, these large J values are not associated with a significant disparity in P–Te bond lengths compared to those found for the alkyl analogues R_3PTe (R = ^iPr , ^nBu , ^tBu) (Sections 6.2 and 6.3, Table 3). On the other hand, the dimer $[\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{PTe}]_2$ (**1**), which incorporates two types of P^{V} –Te bonds (terminal and bridging), exhibits P–Te distances that differ by ca. 0.1 Å and divergent $^1J(^{31}\text{P}, ^{125}\text{Te})$ values of 1500 and 1026 Hz.³⁰

The bond lengths in acyclic or cyclic systems that incorporate a P^{III} –Te bond are in the range 2.46–2.58 Å and they are associated with much smaller $^1J(^{31}\text{P}, ^{125}\text{Te})$ values typically in the range 200–575 Hz; however, there is no correlation between $^1J(^{31}\text{P}, ^{125}\text{Te})$ and $d(\text{P}^{\text{III}}\text{--Te})$ for organophosphorus(III) compounds (Section 5.2, Table 1). The tricyclic compounds $\text{RP}^{\text{III}}[\text{TeP}^{\text{V}}(\text{N}^t\text{Bu})(\mu\text{--N}^t\text{Bu})]_2$ (**2**, R = Ad, ^tBu) provide unique examples of the influence of the formal oxidation state of phosphorus in the same molecule on $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling constants. The values are 420 and 1073 Hz for the P^{III} –Te and P^{V} –Te linkages, respectively, despite the equality of the P–Te bond lengths (Section 5.2).¹⁴ As is observed for organophosphorus(V)-tellurium compounds, higher values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ (560–575 Hz) are found for acyclic P^{III} –Te systems in which two amino substituents are attached to the phosphorus atom; this number is reduced to 400–420 Hz for organophosphorus(III)-tellurium rings with organyl substituents on phosphorus.

Smaller values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ in the range 100–400 Hz are exhibited by three-membered $(\text{RP})_2\text{Te}$ rings (telluradiphosphiranes) in which the formal oxidation state of phosphorus is +2 (Section 5.2).^{14, 31–35} Similarly, the intriguing cage system $\text{P}_6\text{C}_4^t\text{Bu}_4\text{Te}$ (**3**), in which the oxidation state of the phosphorus atoms in the P–Te–P unit is lowered by the presence of P–P bonds, exhibits a low $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling of 358 Hz (Section 5.1.2).³⁶ The 1,2,4-tellurodiphosphole **4** is an especially anomalous example; the $^1J(^{31}\text{P}, ^{125}\text{Te})$ value of 1025 Hz is >400 Hz larger than typical

values for acyclic P^{III} -Te=C compounds (Section 5.1.1).²⁴ This fascinating heterocycle is formally a 6 π -electron system suggesting that higher s character in the the P–Te hybrid orbital (the Fermi contact term) may contribute to this abnormality.³⁷

From an NMR perspective the most interesting class of organophosphorus(III)-tellurium compounds incorporate R_2P and TeR' substituents in *peri* positions on an acenaphthene scaffold, e.g. **5**.¹⁸ Such derivatives exhibit weak “through space” phosphorus-tellurium interactions [$(d(P\text{--}Te) = 3.090\text{--}3.205 \text{ \AA})$] that are associated with remarkably large $^1J(^{31}P, ^{125}Te)$ values of 1306–1357 Hz attributed to three-center four-electron bonding (Section 5.3).

Figure 1. Selected organophosphorus-tellurium compounds.

Infrared spectroscopy has been used only to a limited extent for the characterization of organophosphorus-tellurium compounds. The infrared spectra of trialkylphosphine tellurides $R_3P\text{Te}$ ($R = {}^n\text{Pr}$, ${}^n\text{Bu}$, n-pentyl, Cy, n-octyl) have been investigated by Zingaro et al., who reported two absorption bands in the $400\text{--}470 \text{ cm}^{-1}$ region; the lower frequency band at ca. 400 cm^{-1} does not vary with a change of the alkyl group.³⁸ Subsequently, a detailed vibrational analysis of thermally unstable $\text{Me}_3\text{P}\text{Te}$ and its fully deuterated derivative led to the assignment of the P–Te stretching vibration to a band at 376 cm^{-1} .³⁹ The value of the P–Te stretching force constant was found to be

2.20 mdyn Å⁻¹, cf. 3.73 and 2.84 mdyn Å⁻¹ for P–S and P–Se force constants, respectively,³⁹ in good agreement with the trend in calculated bond dissociation energies for P–E bonds (*vide infra*).²⁰ By contrast, Rømme et al. reported stretching frequencies of 490–526 cm⁻¹ for tris(dialkylamino)phosphine tellurides, which are unexpectedly high compared to the values for the corresponding selenides,⁴⁰ in agreement with earlier work by Rächle et al.⁴¹

In some cases mass spectrometry can provide confirmation of the molecular composition of organophosphorus-tellurium compounds, because naturally occurring tellurium is a mixture of seven isotopes: ¹²²Te (2.5%), ¹²³Te (0.9%), ¹²⁴Te (4.6 %), ¹²⁵Te (7.0%), ¹²⁶Te (18.7%), ¹²⁸Te (31.8%) and ¹³⁰Te (34.5%) that give rise to characteristic patterns in the mass spectra. The observation of molecular ion peaks in electron impact or field ionization mass spectra has been especially useful for the identification of organophosphorus(III)-tellurium rings that cannot be crystallized for X-ray analysis.^{14, 32}

3. Binary Phosphorus-Tellurium Species

A characteristic feature of phosphorus-chalcogen chemistry is the existence of an extensive series of cage molecules of the type P₄E_n (E = S, Se) that are based on a P₄ tetrahedron with various numbers of bridging and/or terminal chalcogen atoms.⁴² In the case of sulfur (E = S) the entire series (n = 3–10) is known and the first member P₄S₃ is used in “strike-anywhere” matches. Tellurium analogs of these binary phosphorus-chalcogen systems have not been reported, presumably reflecting the weakness of P–Te bonds. However, the reactions of the elements phosphorus, sulfur and tellurium in the molten state (700 K) followed by extraction with CS₂ gave a mixture of P₄S₃, P₄S₂Te, and P₄STe₂ in the approximate ratio of 160:4:1.⁴³ On the basis of ³¹P NMR spectra it was concluded that tellurium replaces one or two of the bridging sulfur atoms, respectively, in P₄S₃ in the very small amounts of ternary species that are formed.

Binary P–Te species can, however, be stabilized in solid-state materials as manifested by the ternary telluride BaP_4Te_2 , which is prepared by heating a stoichiometric mixture of the three elements at 475 °C.¹³ As illustrated in Figure 2, the crystal structure of BaP_4Te_2 incorporates chains of $[\text{P}_4\text{Te}_2]^{2-}$ dianions comprised of condensed P_6 rings in the chair form, with the tellurium atoms in the 1,4 positions, and two covalent P–Te bonds (2.47 and 2.54 Å).

Figure 2. Section of the ${}^1_{\infty}[\text{P}_4\text{Te}_2]^{2-}$ chain of BaP_4Te_2

Karaghiosoff et al. have shown that the disodium salt of the $[\text{P}_4\text{Te}_2]^{2-}$ dianion (**6**) is generated in solution in 98% yield by the reaction of white phosphorus with Na_2Te_2 in *N*-methylimidazole at ambient temperature (Scheme 1).¹² The ${}^{31}\text{P}$ and ${}^{125}\text{Te}$ NMR spectra of **6** revealed a bicyclo[1.1.0]tetraphosphane (butterfly) structure with *exo* chalcogen atoms resulting from cleavage of one P–P bond of the P_4 tetrahedron via oxidative addition of $[\text{Te}–\text{Te}]^{2-}$. The ${}^1J({}^{31}\text{P}, {}^{125}\text{Te})$ value for **6** is –457 Hz and an unexpectedly large three-bond coupling [${}^3J({}^{31}\text{P}, {}^{125}\text{Te}) = -138 \text{ Hz}$] is also observed for this discrete P–Te anion.

Scheme 1. Synthesis of the $[\text{P}_4\text{Te}_2]^{2-}$ dianion **6**

4. Phosphine Complexes of Tellurium Cations

The cations RTe^+ and Te^{2+} are potentially useful reagents in organic and inorganic tellurium chemistry, respectively, and some success has been achieved in stabilizing these highly electrophilic species (six valence electrons) by coordination to phosphine donors. In 1965 Petragnani and Moura Campos reported the first compound of the type $\text{R}_3\text{PTe}(\text{Ar})\text{X}$ (Ar = 2-naphthyl, X = I).⁴⁴ Thirty-five years later Godfrey et al. prepared the adduct $\text{Ph}_3\text{PTe}(\text{Ph})\text{I}$ (**7**) by treatment of the tetramer $\text{Ph}_4\text{Te}_4\text{I}_4$ with a stoichiometric amount of PPh_3 in diethyl ether; the phosphorus-tellurium bond length in the linear $\text{P}-\text{Te}-\text{I}$ unit of **7** is 2.568(2) Å (Figure 3).⁴⁵

Figure 3. Molecular structure of $\text{Ph}_3\text{PTe}(\text{Ph})\text{I}$ (**7**)

In 1986 Kuhn and Schumann described the reaction of tellurophosphoranes $\text{R}_3\text{P}=\text{Te}$ (R = Me, ^iPr , ^nBu , ^tBu , NMe_2) with methyl iodide to give $[\text{MeTe}(\text{PR}_3)]^+ \text{I}^-$; these phosphine-stabilized MeTe^+ cations, which were characterized by elemental analyses and $^1\text{H}/^{31}\text{P}$ NMR spectra, undergo nucleophilic attack by MeLi to give Me_2Te and free PR_3 .⁴⁶ Subsequently, Sladky and Köllemann obtained the salts $[\text{RTe}(\text{P}^n\text{Bu}_3)]^+ \text{X}^-$ (**8a**, R = 4- FC_6H_4 , X = ClO_4 ; **8b**, R = Me, X = BF_4) as oils upon oxidation of the corresponding ditelluride RTeTeR with a nitrosyl salt followed by treatment of the product with $^n\text{Bu}_3\text{P}$; the $^1J(^{31}\text{P}, ^{125}\text{Te})$ values for **8a** and **8b** are 1071 and 1046 Hz, respectively.⁴⁷

Very recently, two groups have structurally characterized phosphine complexes of aryltellurenyl cations by using different synthetic approaches.^{48,49} Tokitoh et al. employed the

reaction of two equivalents of a trimethylsilyl reagent with a mixed-valent $\text{Te}^{\text{II}}\text{-Te}^{\text{IV}}$ difluoride in the presence of PPh_3 to generate phosphine complexes of an aryltellurenyl cation (**9**) via the thermodynamically favorable elimination of trimethylsilyl fluoride (Scheme 2a); the complexes **9** were also obtained by treatment of an aryltellurenyl halide with AgBF_4 in the presence of PPh_3 .⁴⁸ Beckmann and co-workers utilized the direct reaction of PPh_3 with the cation $[\text{MesTe}(\text{TeMes})_2]^+$ to produce $[\text{MesTe}(\text{PPh}_3)]^+$ as the triflate salt **10** (Scheme 2b), which may also be prepared by treatment of Mes_2Te with triflic acid in the presence of PPh_3 .⁴⁹ The P–Te bond distance in **10** is 2.467 Å and $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1148 \text{ Hz}$,⁴⁹ in reasonable agreement with the J values reported earlier by Sladky (*vide supra*).⁴⁷ The $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling of 1387 Hz reported for **9a**⁴⁸ is significantly higher than those for other aryltellurenyl cations.

Scheme 2. Syntheses of Phosphine Adducts of Aryltellurenyl Cations

Aryltellurenyl cations may also be stabilized via interaction with a *peri*-phosphino substituent on an acenaphthene scaffold.¹⁹ Typical syntheses of such compounds are shown in Scheme 3 and a representative structure is illustrated in Figure 4. The P–Te distances are around 2.5 Å being slightly enlarged as a result of the *peri* arrangement and the delocalization to form a three centre–four electron P–Te⋯I system.

Scheme 3. Synthesis of Intramolecularly-Stabilized Aryltellurenyl Cations

Figure 4. Molecular structure of the intramolecularly stabilized aryltellurenyl cation **11b**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–P9 2.5107(16), Te1...I1 3.342; I...Te1–P9 170.98.

The Te^{2+} cation has been sequestered as the DPPE-chelated complex **12** by Ragogna and co-workers, who used a ligand-exchange protocol (Scheme 4).¹⁷ The mean P–Te distance of 2.48 Å and the $^1J(^{31}\text{P}, ^{125}\text{Te})$ value of 1020 Hz in **12** are similar to the corresponding parameters for phosphine complexes of ArTe^+ cations (*vide supra*). The frontier Kohn-Sham orbitals and electron localization function for **12** reveal two lone pairs on the two-coordinate tellurium center. According

to natural population analysis, the atomic charges are located primarily on the donating phosphorus atoms (Scheme 4).¹⁷ A substantially longer P–Te bond length of 2.604(1) Å associated with a modest $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling of 780 Hz was found for the PCy_3 complex of a 1,2,5-telluradiazolium cation **13** (Scheme 5).⁵⁰

Scheme 4. Synthesis of $[\text{Te}(\text{DPPE})]^{2+}$ Dication (12**)**

Scheme 5. Charge Distribution in Phosphine Complexes of Tellurium Cations

An intriguing example of a phosphine-stabilized tellurium cation was reported in 1987 by Kuhn and co-workers, who showed that the oxidation of $^t\text{Bu}_3\text{PTe}$ with a ferrocenium salt gives the dication $[\text{}^t\text{Bu}_3\text{P}-\text{Te}-\text{Te}-\text{Te}-\text{P}^t\text{Bu}_3]^{2+}$ (**14**).⁵¹ The crystal structure of the SbF_6^- salt of **14** revealed a mean P–Te distance of ca. 2.50 Å, cf. 2.368 Å for $^t\text{Bu}_3\text{PTe}$;⁵² the mean Te–Te bond length of 2.71 Å is in the typical range for single bonds in organic ditellurides $\text{RTe}-\text{TeR}$. On the basis of these structural parameters, the authors suggested that **14** should be considered as a Te_3^{2+} dication coordinated to two phosphine ligands rather than a tellurophosphorane complex of Te^{2+} .⁵¹ Calculations of the electronic structure of **14** are warranted in order to elucidate this dichotomy.

5. Organophosphorus(III)-Tellurium Compounds

The lability of the P–Te bond is strikingly illustrated by the interesting history of organophosphorus(III)-tellurium compounds containing either P^{III}–Te–C or P^{III}–Te–P^{III} linkages. Since the initial success in the characterization of these fickle systems was achieved with acyclic derivatives, a discussion of those compounds precedes an account of the synthesis and structures of cyclic analogs in this section. Table 1 summarizes pertinent structural and NMR data for selected organophosphorus(III)-tellurium compounds, which provide a benchmark for subsequent discussions.

Table 1. Bond Lengths and NMR Data for Organophosphorus(III)-Tellurium Compounds

P-Te Compound	<i>d</i> (P–Te) (Å)	¹ <i>J</i> (³¹ P, ¹²⁵ Te)(Hz) ^a	$\delta^{125}\text{Te}$ (ppm) ^b	Ref.
<u>Acyclic P–Te–C Systems</u>				
^t Bu ₂ PTe- <i>p</i> -tolyl	<i>c</i>	532	–190.8 (d)	55
ⁱ Pr ₂ PTe- <i>p</i> -tolyl	<i>c</i>	495	–234.8 (d)	55
^t Bu ₂ PTeSiMe ₃	<i>c</i>	384	–772(d)	56
[(Me ₃ Si) ₂ C=P] ₂ Te	<i>c</i>	573.3	+1022 (t)	58
[(ⁱ PrMe ₂ Si) ₂ C=P] ₂ Te	<i>c</i>	578.5	+823 (t)	58
(Me ₃ Si) ₂ C=PTeMes	<i>c</i>	638	+646.0 (d)	58
(Me ₃ Si) ₂ C=PTeTIP	<i>c</i>	652.8	+600.1 (d)	58
(Me ₃ Si) ₂ C=PTeMes*	<i>c</i>	701.5	+859.2 (d)	58
<u>Acyclic P–Te–P Systems</u>				
^t Bu ₂ PTeP ^t Bu ₂	<i>c</i>	451	–574 (t)	59,67
ⁱ Pr ₂ PTeP ⁱ Pr ₂	<i>c</i>	420	–276 (t)	61
[{(Me ₃ Si) ₂ CH}] ₂ P] ₂ Te	2.505(2) 2.552(2)	377	<i>c</i>	62
(ⁱ Pr ₂ N) ₂ PTeP(N ⁱ Pr ₂) ₂	2.559(1) 2.576(2)	562	<i>c</i>	63
[(H ₂ C) ₂ (DippN) ₂ P] ₂ Te	2.584(7) 2.587(8)	556	<i>c</i>	64
<u>Metal Complexes</u>				
(CO) ₄ Cr(^t Bu ₂ PTeP ^t Bu ₂)	2.481(1) 2.491(1)	324	+142 (t)	65,66
(CO) ₄ Cr(ⁱ Pr ₂ PTeP ⁱ Pr ₂)	<i>c</i>	243	+1233 (t)	61

<u>Cyclic P–Te–P Systems</u>				
(^t BuP) ₂ Te	<i>c</i>	229	–696 (t)	31,32
(AdP) ₂ Te	2.479(1)	218.4	–818.3	14
(Mes*OP) ₂ Te	2.463(1)	395(332)	+7.7 (t)	14
(Fc*P) ₂ Te	2.512 (1) 2.500(1)	<i>c</i>	–38.7	70
(CF ₃ P) ₃ Te	<i>c</i>	448.5	+470.8	34
(AdP) ₃ Te	2.502(2) 2.516(2)	<i>c</i>	–461.1	14
(CF ₃ P) ₄ Te	<i>c</i>	445.2	+710.1	34
(FcP) ₄ Te	2.503(6)	<i>c</i>	<i>c</i>	14
(TrtPTe) ₃	2.474(3)-2.517(4)	396	+598.9 (m)	14
(Mes*P) ₃ Te	<i>c</i>	442.0	+774.2 (m)	14
AdP ^{III} [TeP ^V (N ^t Bu)(μ-N ^t Bu)] ₂	2.512(3) 2.508(3)	418 (P ^{III}) 1073 (P ^V)	+368.5	14
^t BuP ^{III} [TeP ^V (N ^t Bu)(μ-N ^t Bu)] ₂	<i>c</i>	416 (P ^{III}) 1073 (P ^V)	+423.4	14
<u>Rings and Cages with Low-valent P</u>				
1,2,4-P ₂ TeC ₂ ^t Bu ₂	<i>c</i>	1035, 140 ^d	1383 (dd)	37
1,2,4-P ₂ TeC ₂ ^t Bu ₂ (W(CO) ₅)	2.378(2)	1175, 133 ^d	1373 (dd)	57
P ₆ C ₄ ^t Bu ₄ (μ-Te)	2.473(1) 2.479(1)	358, 57 ^d	+424.8 (tt)	36
(μ-TeTe)[P(μ-NTer)] ₂	2.600(2) 2.614(2)	<i>c</i>	+287.5 (s)	71

^a Absolute values (magnitude only) taken from ¹²⁵Te NMR spectra where available; ¹J(³¹P, ¹²³Te) data from ³¹P NMR spectra are given *in italics*

^b Ref. Me₂Te (external); d = doublet; t = triplet; dd= doublet of doublets; m = multiplet

^c Not reported

^d ²J(³¹P, ¹²⁵Te)

5.1 Acyclic Organophosphorus(III)-Tellurium Compounds

5.1.1 With P–Te–C Linkages

The first organophosphorus(III)-tellurium compound of the type R₂PTeR' (tellurophosphinites) was reported in 1979 by Grobe et al.⁵³ The derivative (CF₃)₂PTeMe (**15a**) was

obtained as an orange oil from the slow redistribution of $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$ and MeTeTeMe (eq 1) and characterized by ^1H , ^{19}F and ^{31}P NMR spectra and the formation of the chromium complex $\text{Cr}(\text{CO})_5(\text{CF}_3)_2\text{PTeMe}$ upon photolysis in a THF solution of $\text{Cr}(\text{CO})_6$.⁵⁴ Subsequently, du Mont and co-workers prepared aryl tellurophosphinites $\text{R}_2\text{PTe-}p\text{-tolyl}$ (**15b**, $\text{R} = ^i\text{Pr}$; **15c**, ^tBu) in a similar manner; these yellow liquids exhibit a doublet in the ^{125}Te NMR spectra with $^1J(^{31}\text{P}, ^{125}\text{Te})$ values of 495 Hz and 532 Hz, respectively (Table 1).^{55,56} Examples of metal complexes of the isomeric anions $[\text{RPTeAr}]^-$ and $[\text{R}_2\text{PTe}]^-$ are discussed in Section 7.2.

The 1,2,4-tellurodiphosphole **4** also incorporates a C–P–Te functionality. This fascinating heterocycle, which is formally a six π -electron system, is obtained as a yellow oil by reaction of $[\text{Li}(\text{TMEDA})_2][\text{SbP}_2\text{C}_2^t\text{Bu}_2]$ with $\text{Te}(\text{S}_2\text{CNet}_2)_2$ in DME.³⁷ The heterocycle **4** readily forms the P -bonded $\eta^1\text{-W}(\text{CO})_5$ complex **16** as illustrated in Scheme 6.⁵⁷ Although the free ligand **4** has not been structurally characterized, the five-membered ring in **16** is planar and exhibits a short phosphorus-tellurium bond [$d(\text{P-Te}) = 2.378(2)\text{\AA}$]. The $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling of 1175 Hz in **16** is ca. 140 Hz larger than that in **4** (Table 1).³⁷ The latter value is >400 Hz higher than typical values for acyclic $\text{P}^{\text{III}}\text{-Te=C}$ systems (*vide infra*); higher s character in the P–Te hybrid orbital may contribute to this discrepancy for the cyclic system.

Scheme 6. Synthesis of a Tungsten Complex of a 1,2,4-Tellurodiphosphole

The du Mont group has also prepared acyclic compounds incorporating the unsaturated C=P–Te functionality.⁵⁸ Tellurobis(phosphaalkenes) Te(P=CR₂)₂ (**17a** and **17b**) are generated by the reaction of a *P*-chlorophosphaalkene with a disilyltelluride (eq 2). *P*-aryltellurophosphaalkenes (iPrMe₂Si)₂C=P–TeAr (Ar = Ph, Mes, TIP, Mes*) (TIP = 2,4,6-ⁱPr₃C₆H₂) were also prepared via metathesis of the bulky *P*-chlorophosphaalkene (R = ⁱPr) with lithium aryltellurolates.⁵⁸ The ¹J(³¹P, ¹²⁵Te) couplings for the C=P^{III}–Te unit are in the range 570-700 Hz (Table 1).

5.1.2 With P–Te–P Linkages

The first acyclic organophosphorus(III)-tellurium compound with a P–Te–P grouping, ^tBu₂P–Te–P^tBu₂ was reported by du Mont in 1980.⁵⁹ The initial synthesis involved the insertion of tellurium (in the form of either the element or the reagent TePⁿBu₃) into the P–E bond of ^tBu₂P–EMe₃ (E = Si, Ge, Sn). The short-lived insertion products ^tBu₂P–Te–EMe₃ were characterized in situ by multinuclear NMR spectroscopy, ¹J(³¹P, ¹²⁵Te) = 348-384 Hz, but they undergo a rapid redistribution to give ^tBu₂P–Te–P^tBu₂ **18a** and Te(EMe₃)₂ (Scheme 7a).⁵⁹ The telluride **18a** is preferably prepared in 80% yield as pale yellow needles via metathesis (Scheme 7b).⁵⁹ The *tert*-butyl derivative **18a** and the isopropyl analog ⁱPr₂P–Te–PⁱPr₂ (**18b**) may also be prepared via tellurium insertion;^{60,61} the telluride **18b** is also obtained via metathesis (Scheme 7b).⁵⁹ In contrast to **18b**, the isopropyl derivative exists in solution in equilibrium with the diphosphine ⁱPr₂P–PⁱPr₂ and elemental tellurium.⁶¹ Recently, Cowley and co-workers have shown that the congener R₂P–Te–PR₂ (**18c**, R = CH(SiMe₃)₂) is obtained in 31% yield from reaction of the persistent phosphinyl radical •P[CH(SiMe₃)₂]₂ with tellurium in toluene at ambient temperature; the P–Te–P bond angle is 94.87(8)° (Figure 5a).⁶²

Scheme 7. Synthesis of ^tBu₂P–Te–P^tBu₂ (**18a**)

In an alternative approach, Niecke et al. obtained the acyclic derivative $(\text{R}'_2\text{N})_2\text{P}-\text{Te}-\text{P}(\text{NR}'_2)_2$ (**19a**, $\text{R}' = ^i\text{Pr}$) in 44% yield via slow insertion of elemental tellurium (6 days) into the P–P bond of $(^i\text{Pr}_2\text{N})_2\text{P}-\text{P}(\text{N}^i\text{Pr}_2)_2$ in toluene.⁶³ Very recently, a bulky analog $(\text{RR}'\text{N})_2\text{P}-\text{Te}-\text{P}(\text{NRR}')_2$ (**19b**, $\text{R} = \text{Dipp}$, $\text{R}' = -\text{CH}_2-$) was isolated as colorless crystals in 82% yield from a similar, but more rapid (16 h in THF), tellurium-insertion process.^{64,65} Crystal structure determinations of **19a** (Figure 5b) and **19b** confirmed the acyclic arrangement with long P–Te bonds of 2.56 Å (**19a**)⁶³ and 2.59 Å (**19b**)⁶⁴ and narrow P–Te–P bond angles of 94.5° for **19a**, cf. 100° for the sulfur analog,⁶³ and 83.0(2)° for **19b**. The $^1J(^{31}\text{P}, ^{125}\text{Te})$ values for acyclic $\text{P}^{\text{III}}-\text{Te}-\text{P}^{\text{III}}$ compounds are in the range 375–560 Hz (Table 1), significantly smaller than those of $\text{C}=\text{P}^{\text{III}}-\text{Te}$ systems (*vide supra*).

Figure 5. Molecular structures of (a) $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PTeP}[\text{CH}(\text{SiMe}_3)_2]_2$ (**18c**) and (b) $(^i\text{Pr}_2\text{N})_2\text{PTeP}(\text{N}^i\text{Pr}_2)_2$ (**19a**).

An intriguing example of tellurium insertion into a P–P bond is provided by the reaction of the element with the hexaphosphaprismane $\text{P}_6\text{C}_4^t\text{Bu}_4$ in toluene at 60 °C to give the polycyclic compound **3** [$d(\text{P}-\text{Te}) = 2.479(1)$ Å, $^1J(^{31}\text{P}, ^{125}\text{Te}) = 358$ Hz], which is remarkably stable towards air and moisture and thermally robust (Scheme 8).³⁶

Scheme 8. Insertion of Tellurium into a P–P Bond

There have been only limited investigations of the coordination behavior of $R_2P\text{--}Te\text{--}PR_2$ ligands and in all cases *P,P*-chelated complexes are formed. For example, **18a** or **18b** react with $(\eta^4\text{-C}_7\text{H}_8)\text{M}(\text{CO})_4$ ($M = \text{Cr}, \text{Mo}$) or $\text{W}(\text{CO})_4(\text{MeCN})_2$ to give the complexes $[(\text{CO})_4\text{M}\{(\text{PR}_2)_2\text{Te}\}]$ (**20a**, $R = \text{tBu}$, $M = \text{Cr}, \text{Mo}, \text{W}$; **20b**, $R = \text{iPr}$, $M = \text{Cr}$) in good yields.⁶⁶⁻⁶⁸ The $P\text{--}Te\text{--}P$ bond angle in the four-membered CrPtTeP ring of **20a** ($M = \text{Cr}$) is constrained to 81.4° as a result of *P,P*-chelation (Figure 6).⁶⁶ The $^1J(^{31}\text{P}, ^{125}\text{Te})$ values for **18a** and **18c** are reduced substantially (by 127 and 177 Hz, respectively) upon complexation to chromium (Table 1). Reactions of **18a** with either $(\text{PhCN})_2\text{PtCl}_2$ in CH_2Cl_2 or PtCl_2 in toluene produce $[\text{Cl}_2\text{Pt}\{(\text{P}^t\text{Bu}_2)_2\text{Te}\}]$; the ^{31}P NMR spectrum of this platinum(II) complex exhibits coupling constants of $J(^{195}\text{Pt}, ^{31}\text{P}) = 3282 \text{ Hz}$ and $J(^{125}\text{Te}, ^{31}\text{P}) = 325 \text{ Hz}$, consistent with *P,P*-chelation of the ligand to platinum.⁶⁹

Figure 6. Molecular structure of $[(\text{CO})_4\text{Cr}\{(\text{P}^t\text{Bu}_2)_2\text{Te}\}]$ (**20a**).

5.2 Organophosphorus(III)-Tellurium Heterocycles

Pioneering studies by the groups of du Mont and Kariaghiosoff disclosed several methods for the synthesis of organophosphorus(III)-tellurium heterocycles of the type $(\text{RP})_x\text{Te}_y$ and provided important information about the influence of the R substituent on the thermal stability of these labile pnictogen-chalcogen ring systems. The approaches employed by these investigators are summarized below:

- (a) Cyclocondensation of $^t\text{Bu}(\text{Cl})\text{P}-\text{P}(\text{Cl})^t\text{Bu}$ with Na_2Te ³¹
- (b) Insertion of tellurium into a P–Si bond of $^t\text{BuP}(\text{SiMe}_3)_2$ ^{31,32}
- (c) Salt or Me_3SiCl elimination from treatment of RPCl_2 [$\text{R} = ^t\text{Bu}, \text{CF}_3, \text{R}'_2\text{N}$ ($\text{R}' = ^i\text{Pr}, \text{Cy}, \text{Ph}$)] with Na_2Te , Li_2Te_2 or $\text{Te}(\text{SiMe}_3)_2$ ³¹⁻³⁴

The products were invariably obtained as mixtures of organophosphorus(III)-tellurium ring systems. However, in many cases, the components of these mixtures could be tentatively identified by solution-state NMR spectroscopy because the spin system for a particular ring size and/or composition, e.g. $(\text{RP})_x\text{Te}$ ($x = 2,3,4$) and $(\text{RP})_x\text{Te}_2$ ($x = 3,4$), gives rise to characteristic ^{31}P and ^{125}Te NMR spectra, which can be simulated to afford spin-spin coupling constants. Derivatives in which the electronegative CF_3 group is attached to phosphorus exhibit higher stability with respect to loss of tellurium in solution compared to analogs where $\text{R} = \text{alkyl}, \text{aryl}$ or NR_2 . In one study the three-membered ring $(^t\text{BuP})_2\text{Te}$ (a tellurodiphosphirane) was isolated as a yellow oil after trap-to-trap distillation under vacuum.³¹

In summary, detailed spectroscopic studies by the groups of du Mont and Karaghiosoff led to the identification of two classes of organophosphorus(III)-tellurium heterocycles: (a) three-, four- and five-membered rings containing one tellurium atom $(\text{RP})_x\text{Te}$ ($x = 2,3,4$) and (b) five- and six-membered rings containing two tellurium atoms $(\text{RP})_x\text{Te}_2$ ($x = 3,4$) (Figure 7).³¹⁻³⁴ In contrast to the known organophosphorus-sulfur and selenium ring systems,¹⁻⁶ no evidence was found for

heterocycles containing either a Te–Te bond or a P=Te functionality, i.e. a terminal (*exo*) tellurium atom.

Figure 7. Organophosphorus(III)-tellurium heterocycles $\text{Te}_m(\text{PR})_n$ Adapted from ref. 14.
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Very recently, Nordheider et al. obtained solid-state structural confirmation of examples of 3-, 4-, and 5-membered rings $(\text{RP})_x\text{Te}$ ($x = 2,3,4$) by employing very bulky substituents in the cyclocondensation reactions of RPCl_2 , e.g. $\text{R} = \text{Fc}$, Ad , Mes^*O , Mes^* and CPh_3 , with sodium ditelluride Na_2Te_2 , which was found to be the most effective source of tellurium in these reactions.¹⁴ X-ray crystal structures were obtained for the telluradiphosphirane $(\text{RP})_2\text{Te}$ (**21a**, $\text{R} = \text{OMes}^*$), the telluratriphosphetane $(\text{AdP})_3\text{Te}$ (**22**), and the telluratetraphospholane $(\text{FcP})_4\text{Te}$ (**23**) (Figure 8a-c). In addition, the first example of a tritelluratriphosphorinane $(\text{TrtP})_3\text{Te}_3$ (**24**) was prepared and structurally characterized (Figure 8d).¹⁴ The dramatic increase in the P–Te–P bond angle with ring size for the heterocycles containing one tellurium atom, although expected, is particularly noteworthy: 54.1° ($\text{Mes}^*\text{OP})_2\text{Te}$ (**21a**) $\ll$ 80.4° $(\text{AdP})_3\text{Te}$ (**22**) $\ll$ 104.9° $(\text{FcP})_4\text{Te}$ (**23**). The six-membered P_3Te_3 ring in **24** crystallizes in a chair conformation with P–Te–P bond angles in the range 80.9 – 82.5° and Te–P–Te bond angles of 102.1 – 105.7° ; by contrast, no examples of the

P₃Se₃ ring have been reported. The P–Te bond lengths and pertinent NMR data for **21–24** and related organophosphorus(III)-tellurium heterocycles are summarized in Table 1.

Three-membered P₂Te rings may also be generated by oxidation of a diphosphene RP=PR'. Thus, Tokitoh et al. obtained the unsymmetrical telluradiphosphirane (TbtP)(FcP)Te as an orange solid in 66% yield from reaction of TePⁿBu₃ with the corresponding diphosphene in hot benzene. Interestingly, this telluradiphosphirane exhibited markedly different $J(^{125}\text{Te}, ^{31}\text{P})$ values of 260 and 100 Hz, indicative of a significant influence of the phosphorus substituent on this parameter, but the crystal structure was not reported.³⁵ More recently, however, the same group prepared orange crystals of the symmetrical derivative (Fc*P)₂Te (**21b**, Fc* = 2,5-bis(3,5-di-*t*-butylphenyl)ferrocenyl) by very slow oxidation of Fc*P=PFc* with elemental tellurium in benzene at 70 °C and determined the X-ray structure.⁷⁰ The acute P–Te–P bond angle of 52.21(3)° is similar to the value of 54.1° found for **21a**; $|d(\text{P}–\text{Te})| = 2.506(1)$ Å for **21b**, cf. 2.467 Å in **21a**.¹⁴ The value of $J(^{125}\text{Te}, ^{31}\text{P})$ for **21b** could not be determined owing to the very broad ¹²⁵Te NMR resonance.

Figure 8. Molecular structures of organophosphorus(III)-tellurium heterocycles (a) (Mes*OP)₂Te (**21a**) (b) (AdP)₃Te (**22**) (c) (FcP)₄Te (**23**) (d) (TrtP)₃Te₃ (**24**). Adapted from ref. 14. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA

Schulz and co-workers have recently described the slow reaction (14 days) of the intriguing biradicaloid $[P(\mu\text{-N}^{\text{Ter}})]_2$ (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) with elemental tellurium at 60 °C in THF to give dark green crystals of the tricyclic compound **25** in which a ditellurido ($-\text{Te}-\text{Te}-$) unit bridges the $P^{\text{III}}_2\text{N}_2$ ring (Scheme 9a).⁷¹ The steric strain in the five-membered NP_2Te_2 rings of **25** is evident from the long P–Te bonds (2.60–2.61 Å, Table 1). The tricyclic compounds **2** (Section 2) with a $-\text{Te}-P^{\text{III}}(\text{R})-\text{Te}-$ linkage (R = Ad, ^tBu) between the phosphorus atoms of a $P^{\text{V}}_2\text{N}_2$ ring are obtained from metathesis between $\text{R}(\text{PCl}_2)_2$ and the dianion $[\text{tBuN}(\text{Te})\text{P}(\mu\text{-N}^{\text{tBu}})]^{2-}$ (Scheme 9b); they provide unique examples of the influence of the formal oxidation state of phosphorus on $J(^{125}\text{Te}, ^{31}\text{P})$ values in the same molecule (Section 2, Table 1).¹⁴

Scheme 9. Synthesis of Tricyclic Phosphorus(III)-Tellurium compounds

5.3 Weak Phosphorus(III)⋯Tellurium Interactions

A series of *peri*-substituted phosphorus-tellurium systems $\text{R}'\text{Te}-\text{Acenap}-\text{PR}_2$ ($\text{R}' = \text{Ph}$, *p*-An, Nap, Mes, Tip; R = ^tPr, Ph) exhibiting large “through space” spin-spin coupling constants ($J(^{31}\text{P}, ^{125}\text{Te}) = 1210\text{--}1360$ Hz) have recently been described.¹⁸ These *peri*-substituted phosphorus-tellurium systems were prepared by the addition of organotellurium monohalides to lithiated $\text{R}_2\text{P}-\text{Acenap}-\text{Li}$ systems (Scheme 10). These compounds have P⋯Te separations in the range 3.094–3.205 Å (Figure 9, Table 2), cf. sum of the van der Waals radii of the phosphorus and tellurium atoms is 3.86 Å,²⁵ 4.12 Å²⁶ or 4.40 Å.²⁷ The magnitudes of the $J(^{31}\text{P}, ^{125}\text{Te})$ and $J(^{31}\text{P}, ^{123}\text{Te})$ cannot

be explained by through bond spin-spin coupling constants since couplings through five and six bonds are not expected to give such high values. The observed “through-space” spin-spin coupling was rationalized by an overlap of lone pair orbitals and not a $\text{lp}(\text{X}) \rightarrow \sigma^*(\text{Y}-\text{Z})$ donor-acceptor interaction. The species can be described as demonstrating the “onset” of three-centre four-electron type interactions. Oxidation of the phosphorus atoms by sulfur and selenium resulted in a disappearance of the strong P–Te coupling as lone pair orbitals are no longer available for the interaction with those of the tellurium atom.

Scheme 10. Syntheses of *Peri*-substituted Phosphorus(III)-Tellurium Compounds

Figure 9. Molecular structures of typical *peri*-substituted phosphorus(III)-tellurium compounds **26a** and **26e**. Adapted from ref. 18. Copyright 2015 American Chemical Society.

Table 2. Bond Lengths and NMR Data for *peri*-Substituted Phosphorus-Tellurium Compounds.¹⁸

Compound	$d(\text{P} \cdots \text{Te})$ [Å]	$\delta^{125}\text{Te}$ [ppm]	$J(^{31}\text{P}, ^{125/123}\text{Te})$ [Hz] ^a
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26a	3.131	597.4	1306/1084
26b	3.090	580.9	1323/1096
26c	3.108	483.9	1349/1119
26d	3.205	372.2	1332/1105
26e	3.181	410.8	1213/1006
27	3.094	320.9	1357/1127

^a Experimental coupling constants are given as absolute values (magnitude only), but calculated values are negative

6 ORGANOPHOSPHORUS(V) TELLURIDES

Triorganophosphine(V) tellurides (tellurophosphoranes) $R_3P^{V}Te$ are quintessential P–Te compounds in view of their (a) prominent position in the historical development of phosphorus-tellurium chemistry, (b) wide use as tellurium-transfer reagents in a variety of applications, and (c) role as models for understanding the nature of the $P^{V}=Te$ bond. This section will begin with a discussion of the synthesis, spectroscopic properties, and the molecular and electronic structures of $R_3P^{V}Te$ derivatives as well as related compounds with terminal $P=Te$ functionalities. There follows a description of their redox behavior, coordination complexes and applications as a reactive source of tellurium. A comprehensive account of early work (up to 1996) on the chemistry of phosphine tellurides has been published.⁷²

6.1. Synthesis and Spectroscopic Characterization

Zingaro pioneered the field of organophosphorus(V)-tellurium chemistry more than 50 years ago with the synthesis of ${}^nBu_3P^{V}Te$ by oxidation of nBu_3P with elemental tellurium in boiling toluene.¹⁰ Shortly thereafter, a wide variety of derivatives $RR'_2P^{V}Te$ ($R = R' = Et, {}^nPr, Cy$; $R = Ph, R'$

= ⁿPr, ⁿBu),¹¹ as well as Me₃PTe,⁷³ were prepared in a similar manner. These phosphine tellurides were isolated as air, light and thermally sensitive pale yellow solids, which readily deposit grey elemental Te in solution. The derivatives R₃PTe (R = Cy,⁷⁴ ^tBu⁷⁵), which are obtained in essentially quantitative yields by oxidation of R₃P with grey tellurium at room temperature, are thermally stable both in the solid state and in solutions.⁷⁵

The oxidation of the P^{III} center in R₃P becomes more difficult with the introduction of Ph substituents and, consequently, yields are low for PhR'₂PTe (R' = ⁿPr, ⁿBu).¹¹ A recent manifestation of this influence is provided by the synthesis of the bis(phosphine tellurides) Ph₂P(Te)(CH₂)_nP(Te)Ph₂ (n = 2, 6) and the monotelluride Ph₂P(Te)(CH₂)₄PPh₂ in isolated yields of only 6%;⁷⁶ similarly, the yield of Ph₂MePTe from the reaction of Ph₂MeP and Te_∞ in THF is estimated to be ca. 6% according to ³¹P NMR spectra.⁷⁷ By contrast, the alkyl-substituted analogue Me₂P(Te)(CH₂)₂P(Te)Me₂ was obtained in 51% yield⁷⁸ and the monotelluride ⁱPr₂PCH₂P(Te)ⁱPr₂ is isolated in 98% yield from the direct oxidation of the appropriate P^{III}/P^{III} precursor with elemental tellurium.⁷⁹ Elemental tellurium does not oxidize Ph₃P, but the use of a more reactive source of Te in the form of the tellurocyanate [Ph₄As][TeCN] generates a 1:1 adduct of Ph₃PTe with Ph₃P (Section 6.3).⁸⁰

The introduction of an imino substituent increases the nucleophilicity of the phosphorus center, as first demonstrated by Nöth and Mardersteig in the high-yield synthesis of Ph₃P=NP(Te)Ph₂.⁸¹ Secondary amino substituents, especially those derived from cyclic secondary amines, have an even more dramatic effect on the rate of the reaction of phosphines with elemental tellurium. Thus, reaction times are reduced to a few hours at ca. 50 °C in benzene or cyclohexane for the synthesis of (R₂N)₃PTe (R = Me,^{41,82,83} Et,⁸⁴ R₂N = morpholino, piperidino, pyrrolidino^{40,85}). The latter are readily crystallized (Section 6.2) and exhibit enhanced thermal and air stability compared to their trialkyl analogs. The mixed alkyl/dialkylamino derivative Me(Et₂N)₂PTe and the related bifunctional compound (Et₂N)₂P(Te)(CH₂)₄P(Te)(NEt₂)₂ have also been prepared.⁸⁶

Another compelling example of the influence of phenyl substituents on the reactivity of P^{III} centers towards tellurium is provided by imidobis(phosphines) $HN(PR_2)_2$. Although the $R = Ph$ derivative is unreactive towards Te_∞ , treatment of $HN(P^iPr_2)_2$ with tellurium in n-hexane at 23 °C produces the monotelluride $HP^iPr_2N^iPr_2P^{III}Te$ (**28**) in 87% yield.³⁰ An X-ray structural determination revealed that **28** exists as the P–H tautomer in the solid state (Figure 10a); that isomer is also preferred in solution, as demonstrated by the observation of a doublet characteristic of a P–H functionality ($^1J(^{31}P, ^1H) = 400$ Hz) in the ^{31}P NMR spectrum. The air oxidation of a pale yellow solution of **28** produces small amounts of the unusual ditelluride $[TeP^iPr_2N^iPr_2P^{III}Te-]_2$ (**1**) (Figure 10b), which incorporates two types of P(V)–Te bonds (terminal and bridging) with distances that differ by 0.1 Å and $^1J(^{31}P, ^{125}Te)$ values of 1500 and 1026 Hz;³⁰ the dimer **1** is preferably prepared (in 87% yield) by one-electron oxidation of the corresponding anion with iodine (Section 7.3.2).³⁰

Figure 10. Molecular structures of (a) $HP^iPr_2N^iPr_2P^{III}Te$ (**28**) and (b) $[TeP^iPr_2N^iPr_2P^{III}Te-]_2$ (**1**)

The influence of nitrogen substituents on the ease of formation and stability of the terminal $P=Te$ functionality is also manifested in derivatives based on a cyclodiphosphazane, i.e. a saturated four-membered P_2N_2 ring. Scherer and Schnabl showed that $[MeP^{III}(\mu-N^tBu)]_2$ is oxidized by elemental tellurium in benzene at room temperature (48 h) to give the ditelluride *cis*- $[MeP^V(Te)(\mu-N^tBu)]$ in 8% yield; under similar conditions only the monotelluride was obtained from the unsymmetrical P^{III}/P^{III} derivative $[MeP^{III}(\mu-N^tBu)_2P^{III}Cl]$ and tellurium.⁸⁷ Keat and Thompson

prepared the monotelluride $[\text{Me}_2\text{NP}^{\text{III}}(\mu\text{-N}^t\text{Bu})_2\text{P}^{\text{V}}(\text{Te})\text{NMe}_2]$ in a similar manner.⁸⁸ The tellurides based on a *cyclo*- P_2N_2 framework are stable both in the solid state and in solutions.

The Mössbauer spectra of R_3PTe compounds have been interpreted to indicate significant s character in the $\text{P}\text{--}\text{Te}$ bond.²⁹ The yellow color of tris(dialkylamino)phosphine tellurides is attributed to a UV absorption band with a maximum at $280\text{--}290\text{ cm}^{-1}$ and a tail in the visible region.⁴⁰ The IR spectra of R_3PTe compounds are discussed in Section 2.

6.2 NMR Spectra and Phosphorus-Tellurium Exchange

The ^{31}P NMR spectra of organophosphorus(V) tellurides exhibit singlets accompanied by ^{125}Te (and ^{123}Te) satellites (Section 2) and the ^{125}Te NMR spectra display doublets as a result of $^{31}\text{P}\text{--}^{125}\text{Te}$ coupling. Pertinent NMR data and phosphorus-tellurium bond distances for phosphine tellurides and related compounds with terminal $\text{P}=\text{Te}$ functionalities are summarized in Table 3; these data provide a yardstick for subsequent discussion of organophosphorus(V)-tellurium compounds. The ^{125}Te NMR spectra exhibit substantial negative shifts (-492 to -837 ppm) with reference to Me_2Te indicating considerable shielding at the Te nucleus.²⁹ The $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling constants fall within the range $1500\text{--}2290\text{ Hz}$; higher values are associated with derivatives in which imino or amino substituents are attached to phosphorus. The highest reported value of 2290 Hz is found for the unsymmetrical derivative $\text{TeP}(\text{OEt})(\text{NEt}_2)_2$, cf. 1964 Hz for $\text{TeP}(\text{OEt})\text{Et}_2$.⁸⁴

From the entries in Table 3 it is evident that this coupling is not observed in some cases owing to rapid phosphorus-tellurium exchange, which may involve P^{III} centers of unreacted phosphine. Indeed, the addition of an excess of the appropriate phosphine R_3P to a solution of R_3PTe results in the collapse of the well-resolved doublet.^{29,75} A manifestation of this process is the acceleration of the UV photolysis of ditellurides RTeTeR (to give R_2Te and Te) by tertiary phosphines, e.g. Ph_2MeP , which occurs via an Ph_2MePTe intermediate.⁸⁹ In early studies, du Mont

and Kroth proposed that this exchange involves linear intermediates of the type $R_3P\cdots Te\cdots PR_3$,⁹⁰ similar to that observed in the solid state for the adduct $Ph_3P=Te\cdots PPh_3$ (Section 6.3).⁸⁰

Table 3. Bond Lengths and NMR Data for Compounds with Terminal P=Te Linkages

P–Te Compound	$d(P-Te)$ (Å)	$^1J(^{31}P, ^{125}Te)(Hz)^a$	$\delta^{125}Te$ (ppm) ^b	Ref.
<u>Organophosphorus(V) Tellurides</u>				
^t Bu ₃ P ^t Te	2.368(4)	1663	–836.5(d)	29
ⁿ Bu ₃ P ⁿ Te	2.368(1)	1730, 1732	–807(d), –803(d)	29, 52
ⁱ Pr ₃ P ⁱ Te	2.363(1)	1735	–1000(d)	52
Et ₃ P ^e Te	<i>c</i>	1743	–875(d)	52
Cy ₃ P ^c Te	2.3632(7)	<i>c</i>	<i>c</i>	74
Ph ₃ P=Te $\cdots$ PPh ₃	2.270-2.424 3.376-3.948	<i>d</i>	–491.8	29, 80
^t Bu ₂ P(Te)NHCy	2.371(1)	<i>c</i>	<i>c</i>	95
Me ₂ P(Te)(CH ₂) ₂ P(Te)Me ₂	2.357(2)	<i>d</i>	<i>d</i>	78
Ph ₂ P(Te)(CH ₂) ₂ P(Te)Ph ₂	2.363(1)	<i>d</i>	–653(s)	76
Ph ₂ P(Te)(CH ₂) ₄ PPh ₂	2.349(1) 2.242(1)	<i>d</i>	–636.5(s)	76
Ph ₂ P(Te)(CH ₂) ₆ P(Te)Ph ₂	2.365(1) 2.377(1)	<i>d</i>	–641.4(s)	76
ⁱ Pr ₂ PCH ₂ P(Te) ⁱ Pr ₂	2.360(1)	1735	–940.3(d)	79
TeP ⁱ Pr ₂ NP(H) ⁱ Pr ₂	2.380(1)	1642	–846(dd)	30
TeP ⁱ Pr ₂ NP(I) ⁱ Pr ₂	2.378(1)	1758	–723(d)	106
TeP ^t Bu ₂ NP(I) ^t Bu ₂	2.401(1)	1750	–596(d)	106
[TeP ⁱ Pr ₂ N ⁱ Pr ₂ P ^t Te–] ₂	2.394(2)	1500	<i>d</i>	30

	2.489(2)	1026		
(Me ₂ N) ₃ P ^{IV} Te	<i>c</i>	2095,2105 2045(1709)	−822(d), −826(d) <i>d</i>	29,52 82
[O(CH ₂ CH ₂) ₂ N] ₃ P ^{IV} Te	2.357(1)	2153	−813(d)	29,52
[(CH ₂ CH ₂) ₂ N] ₃ P ^{IV} Te	2.355(3)	<i>c</i>	<i>d</i>	85
(^t Bu ₂ Im=N)Ph ₂ P ^{IV} Te ^e	2.372(2)	2245	<i>c</i>	98
<u>Cyclo-P₂N₂ Derivatives</u>				
[^t Bu(H)N(Te)P ^V (μ-N ^t Bu) ₂ P ^{III} N(H) ^t Bu]	2.370(1)	2010	−188(d)	105
Mg[^t BuN(Te)P ^V (μ-N ^t Bu) ₂ P ^{III} N ^t Bu]	2.385(3)	1851	−137(d)	105
^t BuP ^{III} (μ-NMe) ₂ P ^V (Te) ^t Bu	2.354(7)	<i>d</i>	<i>d</i>	107
<i>Cis</i> -[^t BuP(Te)(μ-NMe)] ₂	2.288(5) 2.322(5)	<i>c</i>	<i>c</i>	96
<i>Trans</i> -[^t BuP(Te)(μ-NMe)] ₂	2.327(2)	<i>c</i>	<i>c</i>	96
<u>Metal Complexes</u>				
W(CO) ₅ (TeP ^t Bu ₃)	2.439(2)	1600	−770(d)	99
Cr(CO) ₅ (TeP ^t Bu ₃)	<i>c</i>	1502	−635(d)	99
Mo(CO) ₅ (TeP ^t Bu ₃)	<i>c</i>	1602	−749(d)	99
[FeCp(CO) ₂ (TePMe ₃)]BF ₄	<i>c</i>	1333	−462.6(d)	100
[FeCp(CO) ₂ (TeP ⁱ Pr ₃)]BF ₄	<i>c</i>	1410	−781.8(d)	100
[FeCp(CO) ₂ (TeP ^t Bu ₃)]BF ₄	<i>c</i>	1480	−531.9(d)	100
[FeCp(CO) ₂ {TeP(NMe ₂) ₃ }]BF ₄	<i>c</i>	2086	−825.8	100
[Ag ₂ (NMs ₂) ₂ (^t Pr ₃ P ^{IV} Te) ₂]	2.40-2.43	1419 (1176)	<i>c</i>	103
[Ag ₂ (NMs ₂) (ⁱ Pr ₃ P ^{IV} Te) ₄][NMs ₂]•MeCN	2.40-2.43	1452 (1204)	<i>c</i>	103

[Ag ₂ (¹ Pr ₃ P ⁿ Te) ₂][SbF ₆]	2.40-2.43	1435	<i>c</i>	103
Cd[ⁿ Bu ₃ P ⁿ Te] ₄ (ClO ₄) ₂	<i>c</i>	1317	-715(d)	102
Cd[(Me ₂ N) ₃ P ⁿ Te] ₄ (ClO ₄) ₂	<i>c</i>	1674	-630(d)	102
Cd[Pip ₃ P ⁿ Te] ₄ (ClO ₄) ₂ ^f	<i>c</i>	1710	-550(d)	102
Cd[Pyrr ₃ P ⁿ Te] ₄ (ClO ₄) ₂ ^f	<i>c</i>	1632	-594(d)	102
CdCl ₂ [ⁿ Bu ₃ P ⁿ Te] ₂	<i>c</i>	1287	-720(d)	102
CdCl ₂ [(Me ₂ N) ₃ P ⁿ Te] ₂	<i>c</i>	1617	-728(d)	102
CdCl ₂ [Pip ₃ P ⁿ Te] ₂ ^f	<i>c</i>	1587	-782(d)	102
CdCl ₂ [Pyrr ₃ P ⁿ Te] ₂ ^f	<i>c</i>	1580	-665(d)	102
<i>Dihalides</i>				
Et ₃ P ⁿ TeCl ₂	2.466(1)	1390(1152)	+766(d)	97
Et ₃ P ⁿ TeBr ₂	2.473(1)	1315(1091)	+627(d)	97
Et ₃ P ⁿ TeI ₂	2.490(1)	1251(1038)	+331(d)	97

^a Coupling constants are taken from ¹²⁵Te NMR spectra where available and reported as absolute values (magnitude only). ¹J(³¹P, ¹²³Te) values given in parentheses are taken from ³¹P NMR spectra; s = singlet, d = doublet, dd = doublet of doublets

^b Chemical shifts are reported relative to Me₂Te as external reference

^c Not reported

^d Not available owing to insolubility and/or rapid exchange processes

^e ^tBu₂Im = 1,3-di-tert-butyl-imidazolin-2-ylidene

^f Pip = piperidino; Pyrr = pyrrolidino

Cyclodiphosphazane tellurides that incorporate both P^V and P^{III} sites provide an opportunity to determine whether the phosphorus-tellurium exchange process is inter- or intra-molecular.^{87,88} In an early example, Scherer and Schnabl demonstrated that the monotelluride $[^t\text{Bu}P^{III}(\mu\text{-NMe})_2P^V(\text{Te})^t\text{Bu}]$ (**29**) (Figure 11) undergoes fast site exchange, but they were unable to distinguish between an intermolecular or intramolecular process on the basis of the concentration-dependence of the coalescence temperature.⁹¹ Very recently, Elder et al. carried out a detailed variable-temperature and variable-concentration multinuclear NMR spectroscopic study of the acyclic P^{III}/P^V monotelluride $^i\text{Pr}_2\text{PCH}_2\text{P}(\text{Te})^i\text{Pr}_2$ (**30**) (Figure 11), which showed that the exchange process is *intermolecular* (Figure 12) and occurs with an activation energy of $21.9 \pm 3.2 \text{ kJ mol}^{-1}$; the experimental value was corroborated by DFT calculations which gave a value of 20.4 kJ mol^{-1} .⁷⁹ In a recent book chapter on dynamic NMR, Bain has described this process “as an excellent example of intermolecular exchange”, since it provides a very clear demonstration that the rates depend linearly on concentration.⁹²

Figure 11. Phosphine tellurides with both P^{III} and P^V centers

Figure 12. Intermolecular exchange of tellurium between P^{III} and P^V sites in **30**

6.3 X-ray Structures

A listing of compounds with terminal P=Te functionalities that have been structurally characterized is included in Table 3. Typically, monotellurides of the type $R_3P\text{Te}$ adopt distorted tetrahedral structures with P–Te bond lengths in the range 2.35–2.40 Å.^{53,79,93–95} A few bis(phosphine tellurides) have also been structurally characterized (e.g. **31a,b** and **32** in Figure 13).^{76,78,96}

Figure 13. Molecular structures of (a) *cis*-[^tBuP(Te)(μ-NMe)]₂ (**31a**) (b) *trans*-[^tBuP(Te)(μ-NMe)]₂ (**31b**) and (c) Ph₂P(Te)(CH₂)₆P(Te)Ph₂ (**32**).

The most intriguing structure involves the bright yellow 1:1 adduct of triphenylphosphine telluride and triphenylphosphine Ph₃P=Te⋯PPh₃ (**33**), which exhibits a linear, but markedly asymmetric, P–Te–P configuration with bond lengths in the ranges 2.270–2.424 and 3.376–3.948 Å⁸⁰ (sum of the van der Waals radii for Te = 3.86 Å,²⁵ 4.12 Å²⁶ or 4.40 Å²⁷). Intermolecular phosphorus-tellurium interactions between P^{III} and P^V sites are not observed in the solid state for **30**, but the linear arrangement in this adduct is reminiscent of the proposed intermediate in the phosphorus-tellurium exchange process (Figure 12).

6.4 Bonding and Electronic Structure

The nature of bonding of the phosphorus-tellurium bond in triorganophosphine tellurides $R_3P\text{Te}$ has been a matter of debate. In early studies a bond order of ca. 1.5 was suggested by Kuhn et al. on the basis of P–Te bond lengths.⁹⁴ On the other hand, solution and solid-state ¹²⁵Te NMR and Mössbauer

spectroscopic data have been interpreted by Jones and Sharma to indicate the absence of multiple bonding.²⁹ The DFT calculations of Ziegler et al. for the model compounds Me₃PE (E = O, S, Se, Te) provide some insights into the nature of the formal P=Te double bond as well as a rationale for the thermodynamic lability of the tellurium derivative.²⁰ The phosphorus-chalcogen bond in these chalcogenides is comprised of a σ and two π components that can be represented by resonance structures **A** and **B**, respectively (Figure 14). The two π contributions result from hyperconjugative back-donation from the chalcogen p orbitals to σ^* orbitals on the R₃P fragment. The σ -bond component decreases dramatically down the series O>S>Se>Te, whereas the π -bond orders are only attenuated slightly. The combination of these bonding effects results in calculated P–E bond energies of approximately –544, –337, –266 and –184 kJ mol^{–1}, thus accounting for the thermal and photochemical instability of compounds with terminal P–Te bonds. The relative contributions of the resonance structures **A** and **B** will be strongly influenced by the nature of the R substituents attached to phosphorus, as indicated by the range of values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ given in Table 3.

Figure 14. Resonance structures and one of the π -back bonds for R₃PTe. Adapted from ref.162.
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6.5 Reaction with Electrophiles and Redox Behavior

Kuhn and Schumann demonstrated that triorganophosphine tellurides R₃PTe (R = Me, ⁱPr, ⁿBu, ^tBu, NMe₂) react with methyl iodide in benzene to produce the tellurophosphonium cations [R₃P–TeMe]I in high yields.⁴⁶ The structure of the tritelluro dication [^tBu₃P–Te–Te–Te–P^tBu₃]²⁺

(**14**) ($\angle \text{Te}-\text{Te}-\text{Te}$ $109.0(1)^\circ$, Figure 15a) produced by oxidation of ${}^t\text{Bu}_3\text{PTe}$ with a ferrocenium salt (eq 3)⁵¹ has been discussed in connection with phosphine-stabilized tellurium cations in Section 4. By contrast, Chivers and Konu have shown that the oxidation of Et_3PTe with SO_2Cl_2 or I_2 produce the dihalides Et_3PTeX_2 (**34a**, $\text{X} = \text{Cl}$; **34c**, $\text{X} = \text{I}$) (eq 4 and 5); the corresponding dibromide **34b** ($\text{X} = \text{Br}$) is prepared by halogen exchange between **34a** and Me_3SiBr (eq 6).⁹⁷ The TeX_2 moiety in the weakly associated dimers $(\text{Et}_3\text{PTeX}_2)_2$ is almost linear ($\angle \text{X}-\text{Te}-\text{X} = 171.0^\circ$, $\text{X} = \text{Cl}$; 173.2° , $\text{X} = \text{Br}$; 176.8° , $\text{X} = \text{I}$); the structure of **34c** is shown as a representative example in Figure 15b.⁹⁷ The $\text{P}-\text{Te}$ distances in **14** and **34a-c** are similar at 2.50 and 2.47-2.49 Å, respectively; however, the values of ${}^1J({}^{31}\text{P}, {}^{125}\text{Te})$ become significantly smaller as the electronegativity of the halogen X decreases: 1390, 1315 and 1251 Hz for **34a**, **34b** and **34c**, respectively (Table 3).⁹⁷ Unfortunately, ${}^1J({}^{31}\text{P}, {}^{125}\text{Te})$ has not been reported for the dication **14**.

Figure 15. Molecular structures of (a) $[\text{tBu}_3\text{P}-\text{Te}-\text{Te}-\text{Te}-\text{P}^t\text{Bu}_3]^{2+}$ (**14**, SbF_6^- salt) and (b) $(\text{Et}_3\text{PTeI}_2)_2$ (**34c**).

6.6 Coordination Complexes

Although the lability of the phosphorus-tellurium bond has restricted the development of coordination chemistry, it has been shown that R_3PTe ligands may fulfill either a terminal or a bridging role in metal complexes. The first examples of the former coordination mode were reported in 1985 by Kuhn et al., who generated $\text{M}(\text{CO})_5(\text{TeP}^t\text{Bu}_3)$ ($\text{m} = \text{Cr}, \text{Mo}, \text{W}$) by photolysis of $\text{M}(\text{CO})_6$ in the presence of $^t\text{Bu}_3\text{PTe}$ in THF and determined the X-ray structure of the tungsten derivative **35** (Figure 16a).⁹⁹ Upon coordination the P–Te bond length increases by ca. 0.07 Å and, concomitantly, the $^1J(^{31}\text{P}, ^{125}\text{Te})$ value is reduced by ca. 65 Hz. The P–Te–W bond angle in **35** is 120.1(1)°, which was interpreted to indicate a strong tellurium-tungsten π -donor interaction.⁸⁴ A similar type of π -bonding was invoked for the cationic complexes $[\text{FeCp}(\text{CO})_2(\text{TePR}_3)]^+$ ($\text{R} = \text{Me}, ^i\text{Pr}, ^t\text{Bu}$) on the basis of NMR data.¹⁰⁰

A bridging role for R_3PTe ligands was first demonstrated by Zingaro and co-workers in the dimeric cation $[\{\text{Hg}(\text{TeP}^n\text{Bu}_3)\}_3\text{Br}_5]^{2+}$ (**36**), which was prepared in good yield by reaction of a suspension of elemental tellurium with $^n\text{Bu}_3\text{P}$ and HgBr_2 in boiling acetone.¹⁰¹ The monomeric units in **36** incorporate a six-membered Hg_3Te_3 ring with $d(\text{P}-\text{Te})$ in the range 2.444(9)-2.479(10) Å (Figure 16b). In alkaline solution **36** decomposes to give HgTe . Very recently, a series of

cadmium(II) complexes of phosphine tellurides with a 1:4 stoichiometry $[\text{Cd}(\text{R}_3\text{PTe})_4][\text{X}]_2$ ($\text{R} = {}^n\text{Bu}$, NMe_2 , Pip , Pyrr , Mor ; $\text{X}^- = \text{Cl}^-$, ClO_4^-) have been characterized by elemental analyses and multinuclear NMR spectra; the Cd–Te linkages in these adducts are evinced by the observation of $^1J(^{113}\text{Cd}, ^{125}\text{Te})$ couplings of 878–1040 Hz.¹⁰² The values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ are reduced by ca. 400 Hz in these Cd complexes compared to those in the free ligands (Table 3).

Complexes of triorganophosphine tellurides with coinage metal halides MCl ($\text{M} = \text{Cu}$, Ag) decompose readily with the formation of tellurium, however du Mont and co-workers have structurally characterized several Ag(I) complexes by using Ms_2N^- (di(methylsulfonyl)amide) or SbF_6^- counter-ions, e.g. the dimer $[\text{Ag}_2(\text{Ms}_2\text{N})_2(\mu\text{-}^i\text{Pr}_3\text{PTe})_2]$ (**37**) (Figure 16c).¹⁰³ The $^1J(^{31}\text{P}, ^{125}\text{Te})$ value is reduced by > 300 Hz for this ligand in a bridging role, although the P–Te bond length is only increased by 0.04–0.07 Å.⁸⁸ The special bridging ability of R_3PTe ligands is evinced in the 2:1 complex $[\text{Ag}(\mu\text{-}^i\text{Pr}_3\text{PTe})_2][\text{SbF}_6]$, which forms a cationic coordination polymer.¹⁰³ A 3:1 complex of the $\text{P}^{\text{III}}/\text{P}^{\text{V}}$ monotelluride $[\text{tBu}(\text{H})\text{NP}^{\text{III}}(\mu\text{-N}^t\text{Bu})_2\text{P}^{\text{V}}(\text{Te})\text{N}(\text{H})^t\text{Bu}]$ with AgI has been structurally characterized recently.¹⁰⁴ The three ligands are *Te*-coordinated to AgI and the mean P–Te distance in the complex is only slightly elongated compared to that in the free ligand (Table 3).

Figure 16. Molecular structures of metal complexes of terminal and bridging R_3PTe ligands; (a) $\text{W}(\text{CO})_5(\text{TeP}^t\text{Bu}_3)$ (**35**), (b) $[\{\text{Hg}(\text{TeP}^n\text{Bu}_3)\}_3\text{Br}_5]^{2+}$ (**36**) and (c) $[\text{Ag}_2(\text{Ms}_2\text{N})_2(\mu\text{-}^i\text{Pr}_3\text{PTe})_2]$ (**37**)

6.7 Applications as Tellurium-Transfer Reagents

The lability of the terminal P=Te functionality in phosphine tellurides has been exploited creatively in applications as tellurium-transfer reagents that are soluble and more reactive than elemental tellurium.^{72,108} As mentioned in Section 5.1.2, the use of ⁿBu₃PTe for insertion of Te⁰ into the P–E (E = Si, Ge, Sn) bond of ^tBu₂P–EMe₃ resulted in the formation of the first acyclic P^{III}–Te–P^{III} compound via redistribution of the insertion product ^tBu₂P–Te–EMe₃.⁵⁹ In a series of papers in the late 1980s and early 1990s Steigerwald and co-workers demonstrated the use of phosphine tellurides for the synthesis of a wide variety of transition-metal-tellurium clusters, e.g. [Fe₄Te₄(PR₃)₄] (R = Et, ⁱPr),¹⁰⁹ [Fe₆Te₈(PMe₃)₆]⁷⁸ and [Co₆Te₈(PEt₃)₆].^{110,111} By varying reaction conditions and the ratio of the reagents Co₂(CO)₈ and Et₃PTe, the latter complex was shown to form via the intermediates [CoTe(CO)₂(PEt₃)₂]₂ and [Co₄Te₂(CO)₆(PEt₃)₄].¹¹¹ The final products from reactions of Fe(COT)₂ with Et₃PTe are binary iron tellurides.⁷⁸ Other metal telluride clusters that have been generated by reactions of Et₃PTe with labile transition-metal complexes include: [Pd₆Te₆(PEt₃)₈],¹¹² [Ni₉Te₆(PEt₃)₈],¹¹³ [Ni₂₀Te₁₈(PEt₃)₁₂],¹¹³ [Cr₆Te₈(PEt₃)₆]¹¹⁴ and the ditelluride [(Et₃P)₂(CO)₃MnTe–]₂,¹¹⁵ none of these clusters incorporate intact Et₃PTe ligands.

The versatility of phosphine tellurides as Te-transfer reagents is further manifested in their multifarious applications, e.g. (a) the synthesis of a bridging uranium telluride (eq 7),¹¹⁶ (b) the preparation of terminal transition-metal tellurides (eq 8),¹¹⁷ (c) insertion into metal-metal bonds (eq 9),¹¹⁸ (d) the formation of an η^2 -Te₂^{2–} complex (eq 10),¹¹⁹ and (e) chalcogen-exchange reactions to produce tellurometallates from selenometallates.¹²⁰

The enthalpies of tellurium atom transfer from Cy_3PTe to the molybdenum(III) complex $\text{Mo}(\text{N}^t\text{BuAr})_3$ ($\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) and to the *N*-heterocyclic carbene IPr have been determined by solution calorimetry.⁷⁴ NMR studies showed that the latter process is rapid and quantitative, but the resulting tellurocarbonyl TeIPr was not isolated; the transfer process is slower for Se.⁷⁴ The calorimetric data provided estimates of 322 and 222 kJ mol^{-1} for the bond dissociation enthalpies of the formal $\text{C}=\text{E}$ ($\text{E} = \text{Se}$ and Te , respectively) double bonds in EIPr .

Tellurium insertion into metal-carbon bonds has been investigated in considerable detail.¹²¹⁻
¹²⁷ West and co-workers found that elemental tellurium does not insert directly into the $\text{Mn}-\text{C}$ bond of $\text{RMn}(\text{CO})_5$ ($\text{R} = \text{alkyl, aryl}$) complexes, but the use of $\text{R}'_3\text{PTe}$ ($\text{R} = \text{Me, Et}$) reagents generates the tellurolates $\text{RTeMn}(\text{CO})_3(\text{PR}'_3)_2$ via initial substitution of two CO ligands by PR'_3 followed by Te insertion.¹²² Piers et al. showed that $^n\text{Bu}_3\text{PTe}$ can be employed for Te insertion into the scandium-alkyl bonds of Cp^*_2ScR ($\text{R} = \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{Ph}$), but the tellurolates so formed readily undergo elimination of TeR_2 .¹²³ The use of a stereochemical probe established that both steps in this process occur with retention of configuration, implying concerted transition states for the two reactions (eq 11).^{124,125}

Bridging tellurides can also be generated by reaction of metal hydrides with $^n\text{Bu}_3\text{P}^n\text{Te}$, e.g. the formation of $\text{DpSc}-\text{Te}-\text{ScDp}$ from $[\text{DpScH}]_2$ ($\text{Dp} = \text{meso-Me}_2\text{Si}(\text{}^t\text{BuC}_5\text{H}_3)_2$).¹²⁶ The titanium catalyst Cp^*_2TiH is particularly effective for the heterodehydrocoupling of $^n\text{Bu}_3\text{Sn}$ groups and Te (eq 12).¹²⁷

Phosphine tellurides also provide a reactive source of tellurium in the generation of semi-conducting metal tellurides, which have applications in devices such as solar cells (group 12), infrared detectors (group 14) or room-temperature thermoelectric generators (group 15), as well as biomarkers (group 12). In an early example, CdTe was electrodeposited on a titanium cathode using a solution of TeP^nBu_3 and Cd^{2+} ions in propylene carbonate at ca. 100°C .¹²⁸ In a different approach, pure HgTe was prepared by reaction of $\text{Et}_3\text{P}^n\text{Te}$ with Ph_2Hg in boiling toluene, presumably via the formation of the mercury tellurolate $\text{Hg}(\text{TePh})_2$ via Te insertion into the $\text{Hg}-\text{C}_{\text{aryl}}$ bond; HgTe is also formed by the direct reaction of metallic mercury with TePEt_3 .¹²⁹

In more recent investigations, tri-*n*-octylphosphine telluride (TOPTe) has been shown to be an excellent source of Te^0 ;¹³⁰ much of this work is in the patent literature.¹³¹ Some examples of the applications of TOPTe from the open literature include the preparation of solutions containing CdTe nanoparticles in butanol by reaction with Me_2Cd in the presence of TOP and TOPO ,¹³² as well as the synthesis of the following nanomaterials that are of technological interest: nanocrystalline HgTe ,¹³³ colloidal HgTe quantum dots for mid-IR emission and detection,¹³⁴ hexagonal Bi_2Te_3 nanoplatelets with novel thermoelectric properties,¹³⁵ colloidal PbTe nanocrystals,¹³⁶ CdTe quantum wires,¹³⁷ photoconducting CdTe nanotetrapods,¹³⁸ and CuTe nanocrystals for use as surface-enhanced Raman scattering sensors or photothermal agents.¹³⁹

7 ANIONIC PHOSPHORUS-TELLURIUM LIGANDS

7.1 Tellurophosphates

Potassium O,O'-diethyl tellurophosphate $M[(EtO)_2P(Te)O]$ (**38a**, $M = K$) was obtained as colorless, hygroscopic needles in 1950 by Foss via treatment of potassium diethylphosphite with tellurium in ethanol. The potassium salt **38a** was isolated as “colorless, hygroscopic needles, rapidly darkening in moist air”; no characterization details were given.⁹ Thirty years later Clive and Menchen prepared the Li (**38b**) and Na (**38c**) salts and showed that these phosphorus-tellurium compounds are effective reagents for the deoxygenation of epoxides (eq 13).^{141,142} The reagent **38c** may also be used for the dehalogenation of α -halo ketones.¹⁴³ Although no solid-state structures are available, the anomalously high $^1J(P,Te)$ value of 2115 Hz for **38c**¹⁴² may indicate a short P–Te bond, cf. $(R_2N)_3PTe$ derivatives (Table 3).

7.2 Tellurophosphinites and Ditellurophosphinates

This section describes the anionic species RPTeR^- (**39**),¹⁴⁴ R_2PTe^- (**40**),¹⁴⁵ and $\text{R}_2\text{PTe}_2^{2-}$ (**41**) (Figure 17) which, by analogy with sulfur and selenium analogs,⁸ are potentially interesting ligands.

Figure 17. The anionic species RPTeR^- (**39**), R_2PTe^- (**40**) and $\text{R}_2\text{PTe}_2^{2-}$ (**41**).

The binuclear iron complex $[\text{Fe}_2(\text{CO})_6(\mu\text{-TeMes})\{\mu\text{-P}(\text{iPr})\text{TeMes}\}]$ is a unique example of a complex incorporating an RPTeR^- (**39**) ligand; it exhibits a phosphorus-tellurium bond length of 2.481(5) Å, typical of $\text{P}^{\text{III}}\text{-Te}$ compounds (Table 1), accompanied by both one-bond and two-bond

phosphorus-tellurium couplings, $^1J(\text{P},\text{Te}) = 856 \text{ Hz}$ $^2J(\text{P},\text{Te}) = 353 \text{ Hz}$.¹⁴⁶ The isomeric tellurophosphinito ligand $\text{R}_2\text{P}^-\text{Te}^-$ (**40**) is present in the rhodium complex $[\text{Bupp}_2\text{Ph}_4]\text{Rh}[\eta^2\text{-TePCy}_2]$ ($\text{Bupp}_2\text{Ph}_4 = {}^t\text{BuP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) ($^1J(\text{P},\text{Te}) = 1150 \text{ Hz}$), which is prepared by addition of Te to the Rh-PCy_2 bond.¹⁴⁷ Other complexes containing an $\text{R}_2\text{P}^-\text{Te}^-$ ligand are $\text{CpNi}(\text{TeP}^t\text{Bu}_2)$, identified by mass spectrometry,¹⁴⁸ and $\text{C}_5\text{R}_5\text{W}(\text{CO})_2(\text{TeP}(\text{H})^t\text{Bu})$ ($\text{R} = \text{H}$, $^1J(\text{P},\text{Te}) = 1000 \text{ Hz}$; $\text{R} = \text{Me}$, $^1J(\text{P},\text{Te}) = 980 \text{ Hz}$);¹⁴⁹ the latter was prepared by addition of elemental tellurium to the $\text{W}=\text{P}$ bond of a phosphenium complex.

The anions $\text{R}_2\text{P}^-\text{Te}^-$ (**40a**, $\text{R} = \text{Cy}$; **40b**, $\text{R} = \text{Ph}$) were generated as lithium derivatives in 1990 by Bildstein and Sladky via reaction of $\text{Li}[\text{R}_2\text{P}]$ with elemental tellurium in THF; at that time characterization was limited to ^{31}P and ^{125}Te NMR spectra [$^1J(\text{P},\text{Te}) = 565 \text{ Hz}$ (**40a**), 775 Hz (**40b**)].¹⁵⁰ Chalcogenophosphinates $\text{R}_2\text{P}(\text{Ch})\text{Te}^-$ ($\text{Ch} = \text{O}, \text{S}, \text{Se}$) were also obtained by treatment of $\text{Li}[\text{R}_2\text{P}(\text{Ch})]$ with tellurium, but attempts to prepare $\text{RP}^-\text{Te}_2^{2-}$ by treatment of PhPK_2 with elemental tellurium resulted in a redox process to give the cyclotetraphosphine $(\text{PhP})_4$ and K_2Te .¹⁵⁰ In 2003 Davies and co-workers succeeded in structurally characterizing the monoanions $\text{Ph}_2\text{P}^-\text{Te}^-$ (**40b**) and $\text{Ph}_2\text{P}^-\text{Te}_2^{2-}$ (**41**, $\text{R} = \text{Ph}$) as ion-separated species with THF/TMEDA-solvated Li^+ counter-ions (Figure 18).¹⁵¹ The $^1J(\text{P},\text{Te})$ values of 747 and 1530 Hz for **40b** and **41**, respectively, in these salts provide a cogent illustration of the influence of the formal oxidation state of phosphorus on the magnitude of this parameter (Section 2). The mixed-chalcogen anion $\text{Ph}_2\text{P}(\text{Se})\text{Te}^-$ ($^1J(^{31}\text{P}, ^{125}\text{Te}) = 1485 \text{ Hz}$) was also structurally characterized.¹⁵¹ The structure of the related dianion $[\text{PhP}(\text{Te})_2\text{CH}_2\text{CH}_2\text{P}(\text{Te})_2\text{Ph}]^{2-}$ has been determined in a salt with the octanuclear cluster counter-ion $[\text{Li}_8(\text{OH})_6(\text{THF})_8]^{2+}$.¹⁵²

Figure 18. Molecular structures of $\text{Ph}_2\text{P}^-\text{Te}^-$ (**40b**) and $\text{Ph}_2\text{P}^-\text{Te}_2^-$ (**41**, $\text{R} = \text{Ph}$) in THF/TMEDA-solvated Li^+ salts

In their early work Bildstein and Sladky showed that the reaction of tellurium with diorganylphosphides takes place even when the phosphide is coordinated to a Lewis acid to give the adducts $(\text{L})\text{PR}_2\text{Te}^-$ ($\text{R} = \text{Ph}$, $\text{L} = \text{BH}_3$; $\text{R} = \text{tBu}$, $\text{Cr}(\text{CO})_5$).¹⁵⁰ More recently, Wagner and co-workers obtained the potassium salts of $[(\text{H}_3\text{B})\text{PR}_2\text{Te}]^-$ [$\text{H}_3\text{B}\cdot\mathbf{40}$, $\text{R} = \text{Ph}$, tBu] in almost quantitative yields and structurally characterized the $[\text{K}(18\text{-crown-6})]^+$ adducts; the anionic ligand in the $\text{R} = \text{Ph}$ derivative binds to K^+ through the B atom as well as the Te center.⁷⁷ The high yield of $[(\text{H}_3\text{B})\text{PPh}_2\text{Te}]^-$ is in distinct contrast to the reluctance of the neutral, isoelectronic phosphine H_3CPPh_2 to react with Te_∞ (Section 6.1) and presumably reflects the increased nucleophilicity of the anionic species towards chalcogens (Section 7.3.1).

7.3 Telluroimidophosphinites, Tellurobisimidophosphinates, Mono- and Di-Telluroimidodiphosphinates¹⁵³

7.3.1 Alkali-Metal Derivatives

Similarly to neutral phosphine tellurides (Section 6.1), the introduction of an amido or imido substituent markedly enhances the thermal stability of anionic phosphorus-tellurium species of the type $[\text{R}_2\text{P}(\text{Te})\text{NR}]^-$ (**42**, telluroimidophosphinites), $[\text{RP}(\text{Te})(\text{NR})_2]^{2-}$ (**43**, tellurobisimidophosphonates), $[\text{N}(\text{PR}_2)(\text{PR}_2\text{Te})]^-$ (**44**, telluroimidodiphosphinates), and

$[\text{N}(\text{PR}_2\text{Te})_2]^-$ (**45**, ditelluroimidodiphosphinates) (Figure 19). The coordination chemistry of **45** is particularly extensive.¹⁵

Figure 19. Imidophosphorus-tellurium anions (a) $[\text{R}_2\text{P}(\text{Te})(\text{NR})]^-$ (**42**) $[\text{RP}(\text{Te})(\text{NR}')_2]^{2-}$ (**43**), (b) $[\text{N}(\text{PR}_2)(\text{PR}_2\text{Te})]^-$ (**44**), and $[\text{N}(\text{PR}_2\text{Te})_2]^-$ (**45**).

In view of the relatively low reactivity of neutral phosphines such as $^t\text{Bu}_2\text{PNHR}'$ ($\text{R}' = \text{alkyl}$), $\text{PhP}(\text{NHR}')_2$ and $(\text{Ph}_2\text{P})_2\text{NH}$ towards elemental tellurium (Section 6.1), it is necessary to generate the corresponding anions via deprotonation prior to reaction with elemental tellurium (Te_∞) in order to generate P–Te functionalities. Thus, Bochmann et al. reported that treatment of $\text{Li}[^t\text{Bu}_2\text{PNR}']$ with tellurium powder in THF at 0 °C generates yellow solutions of Li42 ($\text{R} = ^t\text{Bu}$, $\text{R}' = ^i\text{Pr}$, Cy).⁹⁵ By using this “metallation-first” approach, the dilithium derivative $\{[\text{Li}(\text{THF})]_2\text{43}\}_2$ ($\text{R} = \text{Ph}$, $\text{R}' = ^t\text{Bu}$) is obtained in low yield (eq 14).¹⁵⁴ The monomeric units in this dimer incorporate N,N' - and N,Te -coordinated $[\text{Li}(\text{THF})]^+$ cations that are linked through Li–Te contacts to form a central transoid Li_2Te_2 ring, $d(\text{P}–\text{Te}) = 2.4935(12) \text{ \AA}$, $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1212 \text{ Hz}$.

Similarly, Chivers and co-workers showed that the reagents $\text{Na}[\text{N}(\text{PR}_2)_2]$ react with tellurium in hot toluene in the presence of TMEDA to produce sodium salts of the anions $[\text{N}(\text{PR}_2\text{Te})_2]^-$ (**45**, $\text{R} = \text{Ph}$,¹⁵⁵ ^iPr ,¹⁵⁶ ^tBu ¹⁵⁷) (Scheme 11). In the solid state the phenyl derivative exists as a centrosymmetric dimer $\{[\text{Na}(\text{TMEDA})][\text{N}(\text{PPh}_2\text{Te})_2]\}_2$ in which the ligand is Te,Te' -chelated to TMEDA-solvated Na^+ ions and the monomer units are linked by strong Na–Te

interactions to form an approximately square Na_2Te_2 ring.¹⁵⁵ The synthesis of the lithium derivative **Li44** ($\text{R} = \text{}^i\text{Pr}$) by metallation of the monotelluride **28** (Figure 10) with ${}^n\text{BuLi}$ in THF requires low temperatures ($-78\text{ }^\circ\text{C}$) to avoid disproportionation (Scheme 11); under these conditions the telluroimidodiphosphinate **44** ($\text{R} = \text{}^i\text{Pr}$) can be used as an in situ reagent for metathetical reactions (Section 7.3.3).¹⁵⁸ This protocol is also the preferred procedure for the preparation of lithium derivatives of the mixed-chalcogen anions $[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]^-$ ($\text{E} = \text{S}, \text{Se}$) via treatment of **Li44** ($\text{R} = \text{}^i\text{Pr}$) with sulfur or selenium in THF (Scheme 11).¹⁵⁹

Scheme 11. Synthesis of Alkali-Metal Salts of Mono and Ditelluridoimidodiphosphinates.

Adapted from ref. 15. Copyright 2010 American Chemical Society.

The ion-separated salt $\text{Cp}_2\text{Co}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]$ (Figure 20) is obtained by the two-electron reduction of the corresponding cation $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]^+$ with cobaltocene.¹⁶⁰ The related mixed-chalcogen systems $\text{Cp}_2\text{Co}[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]$ are prepared by using a similar synthetic protocol. The ${}^1J({}^{31}\text{P}, {}^{125}\text{Te})$ values of 1540-1570 Hz in these ion-separated salts are ca. 100-125 Hz larger than those in the corresponding lithium derivatives and, consistently, the Te–P bond lengths in the free anions are ca. 0.1 Å shorter. The extremely air-sensitive, ion-separated salt

$[\text{Me}_2\text{Al}(\text{TMEDA})][\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]$, which has been structurally characterized in the solid state, also incorporates the anion **45** ($\text{R} = {}^i\text{Pr}$) and exhibits a similar ${}^1J({}^{31}\text{P}, {}^{125}\text{Te})$ value of 1560 Hz.¹⁶¹

Figure 20. Molecular structure of the $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]^-$ anion **45** ($\text{R} = {}^i\text{Pr}$) in the Cp_2Co^+ salt

7.3.2 Redox Chemistry

The structures of the dimers formed upon one electron-oxidation of the anions $[\text{N}(\text{PR}_2\text{Te})_2]^-$ with iodine are strongly influenced by the nature of the R group. When $\text{R} = {}^i\text{Pr}$, the ditelluride (DT) **1** is formed in which the central Te–Te linkage is elongated by ca. 8%³⁰ compared with the mean value of 2.72 Å (range 2.66–2.78 Å) for typical ditellurides RTe–TeR .¹⁶² DFT calculations for the model system $(\text{TePMe}_2\text{NPM}_2\text{PTe-})_2$ have provided insight into the nature of the Te–Te bond in **1**, which is shown to result from the bonding interaction between the SOMOs of two radicals (Figure 21).

Figure 21. The SOMO-SOMO bonding interaction of two $[\text{TePMe}_2\text{NPMe}_2\text{PTe}]^{\bullet}$ radicals. Adapted from ref. 15. Copyright 2010 American Chemical Society.

By contrast, oxidation of the *tert*-butyl derivative $[\text{N}(\text{P}^t\text{Bu}_2\text{Te})_2]^-$ gives the unique spirocyclic compound **46** (Figure 22).¹⁵⁷ The dimer **46** may be viewed as a contact ion pair (CIP) in which the $[\text{N}(\text{P}^t\text{Bu}_2\text{Te})_2]^-$ anion is *Te,Te'*-chelated to one tellurium atom of the cyclic $[\text{N}(\text{P}^t\text{Bu}_2\text{Te})_2]^+$ cation as a result of an internal redox process. The Te–Te–Te unit in **46** is almost linear with long Te–Te distances of 2.981 and 3.102 Å. The elongation of the Te–Te bond in the five-membered cation is the result of the donation of electron density from the anionic part of the dimer into the LUMO $[\sigma^*(\text{Te}–\text{Te})]$ of the cation (*vide infra*).¹⁵⁷ The anion-cation interaction also results in a disparity of 0.19 Å in the P–Te bond lengths of the cationic part of **46**. Consistent with the experimental findings, DFT calculations of the relative energies of the two structural types reveal that the CIP is more stable than the DT isomer for R = *t*Bu by ca. 20 kJ mol^{–1}, whereas the two structural arrangements are similar in energy for R = *i*Pr.¹⁵⁷ The ³¹P NMR spectrum of **46** exhibits four singlet resonances at low temperature, consistent with the four different phosphorus environments in the solid-state structure,¹⁵⁷ whereas the ³¹P NMR spectrum of the structural isomer **1**, which is a centrosymmetric dimer in the solid state, is comprised of mutually coupled doublets.³⁰

Figure 22. Molecular structure of the spirocyclic contact ion pair $(\text{TeP}^t\text{Bu}_2\text{NP}^t\text{Bu}_2\text{PTe})_2$ (**46**)

Although oxidation of the mixed chalcogen anions $[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]^-$ ($\text{E} = \text{S}, \text{Se}$) does not proceed cleanly, one-electron reduction of the corresponding cyclic cations $[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]^+$ (*vide infra*) with cobaltocene produces the corresponding ditellurides, $(\text{E}^i\text{Pr}_2\text{NP}^i\text{Pr}_2\text{P}^i\text{Te})_2$.¹⁶⁰ The elongation of the Te–Te bond in these mixed chalcogen systems is less pronounced than that in the all-tellurium system because the SOMO of the neutral radicals $[\text{E}^i\text{Pr}_2\text{NP}^i\text{Pr}_2\text{P}^i\text{Te}]^\bullet$ ($\text{E} = \text{S}, \text{Se}$) will be polarized toward the more electropositive tellurium center (Figure 21).

Two-electron oxidation of the anions $[\text{N}(\text{PR}_2\text{Te})_2]^-$ with I_2 produces the corresponding cyclic cations $[\text{N}(\text{PR}_2\text{Te})_2]^+$ with iodide counter-ions.^{163,164} The solid-state structures of these iodide salts depend on the nature of the substituent on the P atoms. Thus, the *isopropyl* derivative **47a** forms an infinite chain of non-planar cations linked by $\text{Te}\cdots\text{I}$ interactions (Figure 23a),¹⁶³ whereas the *phenyl* derivative **47b** is dimeric (Figure 23b).¹⁶⁴ The Te–Te bond lengths in **47a** (2.840 Å) and **47b** (2.846 Å) are slightly elongated as a result of electron donation from the I^- counter-ion into the LUMO $[\sigma^*(\text{Te}-\text{Te})]$ of the cation (Figure 24). In support of this explanation, the replacement of the iodide counterion in **47a** by SbF_6^- produces an ion-separated salt with a typical Te–Te distance of 2.716 Å.¹⁶⁴ The mixed chalcogen cations $[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]^+$, which are prepared by stoichiometric oxidation of the corresponding anions with I_2 , exhibit preferential bonding of the iodide counter-ion to tellurium because the LUMO depicted in Figure 24 is polarized towards the more electropositive chalcogen.¹⁶⁰

Figure 23. Molecular structures of (a) $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\text{I}$ (**47a**) and (b) $[\text{N}(\text{PPh}_2\text{Te})_2]\text{I}$ (**47b**)

Figure 24. The LUMO of the cation $[(\text{NP}^i\text{Pr}_2\text{Te})_2]^+$. Adapted from ref. 15. Copyright 2010 American Chemical Society.

The five-membered cation $[(\text{NP}^i\text{Pr}_2\text{Te})_2]^+$ is formally a 6 π -electron system, but the net π -bond order is close to zero because the bonding effect of the Te–Te π -bonding orbital (HOMO-2) is approximately canceled by the occupation of the Te–Te π^* -antibonding orbital (HOMO); the third occupied π -orbital (HOMO-1) is primarily a nonbonding nitrogen-centered orbital.^{15,163}

7.3.3 p-Block, d-Block and f-Block Metal Complexes

Recent interest in metal complexes of anionic P–Te ligands of the type **42–45** was spurred by the possibility of using them as single-source precursors for the generation of metal telluride thin films or quantum dots (Section 8).¹⁶ In early work Bochmann and co-workers developed methods for the preparation of several thermally stable, homoleptic complexes of **42** with divalent metals (**48**, M = Zn, Cd, Cr, Mn, Fe, Co) via protolysis of the metal amides $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ with a phosphinotelluroic amide (Scheme 12).^{165,166} The complexes **48** were investigated as potential sources of the corresponding binary metal tellurides (Section 8).

Scheme 12. Synthesis of Metal Complexes of Telluroimidophosphinites

Extensive studies of the metathetical reactions of alkali-metal derivatives of the ditelluroimidodiphosphinates **45** (R = *i*Pr) with main group, transition-metal, lanthanide, and actinide halides have generated homoleptic complexes $M[N(\text{P}^i\text{Pr}_2\text{Te})_2]_n$ ^{15,161} with square-planar (**49**, $n = 2$, M = Ni,¹⁶⁷ Pd,¹⁶⁸ Pt¹⁶⁸), distorted tetrahedral (**50**, $n = 2$, M = Zn, Cd, Hg),¹⁵⁶ distorted octahedral (**51**, $n = 3$, M = Sb,¹⁵⁶ Bi,¹⁵⁶ La,¹⁶⁹ U,¹⁶⁹ Pu,¹⁷⁰ Ce¹⁷⁰) or pseudo-trigonal bipyramidal (**52**, $n = 2$, M = Sn,¹⁷¹ Pb¹⁷¹) geometries (Figure 25). In contrast to the monomeric structures of **49-52**, the thallium(I) complex $\{\text{Tl}[N(\text{P}^i\text{Pr}_2\text{Te})_2]\}_\infty$, which is prepared from $[\text{Na}(\text{TMEDA})]\textbf{45}$ and TlOEt, forms infinite chains linked by $\text{Tl}\cdots\text{Te}$ interactions in which six-coordinate Tl centers are bridged by two different $[N(\text{P}^i\text{Pr}_2\text{Te})_2]^-$ ligands arranged approximately perpendicular to each other.¹⁷² The structure of the square-planar tellurium(II) complex $\text{Te}[N(\text{P}^i\text{Pr}_2\text{Te})_2]_2$ has been reported recently.¹⁷³

Figure 25. Metal Complexes of **45 (R = *i*Pr).** Adapted from ref. 15. Copyright 2010 American Chemical Society.

Coinage metal complexes provide a cogent example of the proclivity of the tellurium-centered ligands **45** to adopt a doubly bridging mode.¹⁷⁴ For example, one of the ligands in the trimeric copper(I) complex $\{\text{Cu}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\}_3$ (**53**) exhibits this behavior (Figure 26a). The flexibility of the ditellurido ligands **45** is also evident in the hexameric silver(I) complex $\{\text{Ag}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\}_6$ (**54**), which forms a twelve-membered Ag_6Te_6 ring (Figure 26b).¹⁷⁴ By contrast, a change of the substituents on phosphorus from ^iPr to Ph generates the tetramer $\{\text{Ag}[\text{N}(\text{PPh}_2\text{Te})_2]\}_4$ (**55**) in the form of a centrosymmetric chair-shaped Ag_4Te_4 ring (Figure 26c).¹⁷⁴

Figure 26. Molecular structures of (a) $\{\text{Cu}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\}_3$ (**53**) (b) $\{\text{Ag}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\}_6$ (**54**) and (c) $\{\text{Ag}[\text{N}(\text{PPh}_2\text{Te})_2]\}_4$ (**55**)

The lability of the P–Te bond is illustrated by the outcome of the attempted synthesis of homoleptic complexes of Ga(III), In(III) and Au(I) via metathesis.^{175,176} In all three cases a tellurium-transfer process occurs to give the novel metal-tellurium rings $\{\text{Ga}(\mu\text{-Te})[\text{P}^i\text{Pr}_2\text{PN}^i\text{Pr}_2\text{P}^i\text{Pr}_2\text{Te}]\}_2$ (**56**) (Figure 27a),¹⁷⁵ $\{\text{In}(\mu\text{-Te})[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\}_3$ (**57**) (Figure 27b),¹⁷⁵ and $\{\text{Au}(\mu\text{-Te})[\text{R}_2\text{PNR}_2\text{P}^i\text{Pr}_2\text{Te}]\}_2$ (**58**, R = Ph, ^iPr , ^tBu) (Scheme 13).¹⁷⁶ Both **56** and **58** are formed as a mixture of *cis* and *trans* isomers.^{175,176} Interestingly, in the case of the gold system the tellurium transfer, which involves an intramolecular oxidative addition, can be reversed. Thus, addition of Ph_3P to the Au^{III} complexes **58** produces the Au^{I} complexes $\text{Au}(\text{PPh}_3)[\text{N}(\text{PR}_2\text{Te})_2]$ (**59**) (Scheme

14), which are also formed via metathesis of [Na(TMEDA)]**45** with AuCl in the presence of triphenylphosphine.¹⁷⁶

Figure 27. Group 13 complexes formed by tellurium transfer

Scheme 13. Reversible Tellurium Transfer in Gold Complexes. Adapted from ref. 176.

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Homoleptic group 10 complexes of the mixed chalcogen ligands $M[N(P^iPr_2E)(P^iPr_2Te)]_2$ ($M = Ni, Pd$; $E = S, Se$) are prepared by metathesis between the corresponding Li reagents (Scheme 11) and $NiBr_2(DME)^{177}$ ($DME = \text{dimethoxyethane}$) or $MCl_2(COD)$ ($COD = 1,5\text{-cyclooctadiene}$).¹⁶⁸ The Pd and Pt complexes exist as a mixture of *cis* and *trans* isomers in solution,¹⁶⁸ whereas the Ni^{II} complexes are isolated as the square-planar *trans* isomers.¹⁷⁷ By contrast the closely related mixed chalcogen Ni^{II} complex $Ni[N(P^iPr_2S)(P^iPr_2Se)]_2$ adopts a tetrahedral structure in the solid state.¹⁷⁸

The monotellurido reagent Li**44** ($R = i\text{Pr}$, Figure 19) can be used as an *in situ* reagent at low temperatures for the preparation of homoleptic metal complexes via metathesis (Section 7.3.1).¹⁵⁸ Under these conditions homoleptic complexes of the type $M(\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{P})_2$ with distorted tetrahedral ($M = \text{Zn}, \text{Cd}, \text{Hg}$)¹⁵⁸ or square-planar ($M = \text{Ni},^{177} \text{Pd},^{168} \text{Pt}^{168}$) structures are obtained. The Ni complex is formed exclusively as the *trans* isomer,¹⁷⁷ whereas *cis* and *trans* isomers can be separated by fractional crystallization for the Pd analogue.¹⁶⁸

The trimeric group 11 complexes $[\text{M}(\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{P})]_3$ (**60a**, $M = \text{Cu}$; **60b**, $M = \text{Ag}$) adopt interesting architectures in which the tellurium centers bridge two metal atoms to give highly distorted chair-like M_3Te_3 rings, which readily undergo chalcogen insertion reactions (into the Cu–P bond) to give the mixed-chalcogen complexes $[\text{Cu}(\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{PE})]_3$ (**61a**, $E = \text{O}$; **61b**, $E = \text{S}$; **61c**, $E = \text{Se}$) in which the tellurium sites occupy bridging positions (Scheme 14).¹⁷⁹

Scheme 14. Synthesis of Mixed Chalcogen Complexes $[\text{Cu}(\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{PE})]_3$

7.4 PCP-Bridged Tellurium-Centered Anions

The PCP-bridged anions $[\text{HC}(\text{PR}_2)(\text{PR}_2\text{Te})]^-$ and $[\text{HC}(\text{PR}_2\text{Te})_2]^-$ are formally isoelectronic with the PNP-bridged anions $[\text{N}(\text{PR}_2)(\text{PR}_2\text{Te})]^-$ (**44**) and $[\text{N}(\text{PR}_2\text{Te})_2]^-$ (**45**), which were discussed in Section 7.3.1. In 1987 Lusser and Peringer reported the formation of the lithium reagent $\text{Li}[\text{HC}(\text{PPh}_2)(\text{PPh}_2\text{Te})]$ (**62**) via the metallation-first approach and used it as an *in situ* reagent to prepare the homoleptic mercury complex $\text{Hg}[\text{HC}(\text{PPh}_2)(\text{PPh}_2\text{Te})]_2$ ((Scheme 15).¹⁸⁰ More than 20

years later, Konu and Chivers isolated TMEDA·**62** as a yellow powder in high yield.¹⁸¹ In the solid state **62** exists as a centrosymmetric dimer with an intermolecular Te···Te close contact of 3.514 Å (Figure 28). The calculated bond order indicates that the Li–Te contact approaches a covalent bond with a value of 0.9. The reaction of TMEDA·Li[HC(PPh₂)₂] with two equivalents of tellurium produces the thermally unstable ditelluro anion [HC(PR₂Te)₂][−] (¹J(³¹P, ¹²⁵Te = 1376 Hz), but the lithium derivative could not be isolated in the solid state.¹⁸¹

Scheme 15. Synthesis of Hg[HC(PPh₂)(PPh₂Te)]₂ from **62**

Figure 28. Molecular structure of TMEDA·Li[HC(PPh₂)(PPh₂Te)] (TMEDA·**62**)

7.5 A Carbon-Bridged P–Te–Al Heterocycle

The intriguing, dark red heterocycle **63** is obtained in good yield by oxidation of the P^{III} center in the frustrated Lewis pair (FLP) Mes₂PC(=CHC₆H₅)Al^tBu₂ with tellurium at 100 °C in toluene (Scheme 16).¹⁸²

Scheme 16. Synthesis of the Carbon-Bridged P–Te–Al Heterocycle **63**

In the solid state the structure of **63** (Figure 29) resembles that of TMEDA·**62** (Figure 28) in exhibiting a dimeric structure with a short intermolecular Te···Te contact of 3.33 Å. The P–Te bond length of 2.4651(4) Å is ca. 0.06 Å longer than that in TMEDA·**62**. Consistently, the values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ differ substantially, 938 Hz¹⁸² vs. 1358 Hz.¹⁸¹ The value observed for **63** is notably smaller than those observed for organophosphine tellurides with one-coordinate tellurium (Table 3), but it is comparable to that found for the bridging $\text{P}^{\text{V}}\text{--Te}$ unit in the dimer $(\text{TeP}^{\text{i}}\text{Pr}_2\text{NP}^{\text{i}}\text{Pr}_2\text{P}^{\text{V}}\text{Te})_2$ (**1**) for which $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1026$ Hz and $d(\text{P--Te}) = 2.489(2)$ Å and the Te center is two-coordinate (Section 2 and Table 3). In view of the known difficulties in the synthesis of triarylphosphine tellurides (Section 6.1), and their thermal instability, the high-yield synthesis of **63** is remarkable and suggests that the Al–Te interaction provides a stabilizing influence on the P–Te bond.¹⁸²

Figure 29. Molecular structure of the carbon-bridged P–Te–Al heterocycle **63**

7.6 Tellurium-Centered Anions Supported by a P₂N₂ Ring

7.6.1 Alkali Metal Derivatives

The tellurium-centered dianionic ligand [^tBuN(E)P(μ-N^tBu)₂P(E)N^tBu]²⁻ (**64**, E = Te) resembles the ditellurimidodiphosphinates **44** (Figure 19) with the important difference that the former has a double negative charge. Furthermore, the two tellurium centers in **64** are bridged by a four-membered P₂N₂ ring with exocyclic NR substituents, whereas those in **44** are linked by a PNP unit. Consequently, the dianion **64** may adopt a variety of bonding modes with metal centers as illustrated by the solid-state structures of the alkali-metal derivatives. The dilithium compound [Li(TMEDA)]₂**64** (E = Te) exhibits asymmetric *Te,Te'* and *N,Te* coordination to the Li⁺ ions,¹⁵⁵ whereas the disodium analog [Na(TMEDA)]₂**64** (E = Te) adopts a symmetric *N,N'* and *Te,Te'* arrangement (Figure 30)¹⁸³ reminiscent of the structures of the sulfur and selenium analogs [Na(THF)₂]₂**64** (E = S, Se).^{184,185}

Figure 30. Bonding modes of alkali-metal complexes of **64** (E = Te)

7.6.2 Redox Chemistry

The behavior of the dianions **64** upon oxidation is markedly dependent on the nature of the chalcogen. The two-electron oxidation of $[\text{Na}(\text{THF})_2]_2\textbf{64}$ ($\text{E} = \text{S}, \text{Se}$) with I_2 produces the macrocycles **65** in which a planar P_6E_6 ($\text{E} = \text{S}, \text{Se}$) framework is anchored by perpendicular $\text{P}^{\text{V}}\text{N}_2$ rings (Scheme 17).¹⁸⁶

Scheme 17. Formation of Macrocycles upon Oxidation of $[\text{Na}(\text{THF})_2]_2\textbf{64}$ ($\text{E} = \text{S}, \text{Se}$)

By contrast, the outcome of the I_2 oxidation of **64** ($\text{E} = \text{Te}$) reflects the greater lability of the $\text{P}\text{--}\text{Te}$ bond. Two intermediates have been isolated and structurally characterized, viz. the planar dianionic ditelluride **66**¹⁸³ and the spirocyclic dianion **67** with a central Te_5 motif (Figure 31).¹⁸⁷ The final product is the cyclic tritelluride **68** (Figure 30).¹⁸³ The complex $[\text{Li}(\text{TMEDE})]_2\textbf{66}$ is a rare example of a planar ditelluride. In this case, the planarity is attributed to packing effects,¹⁸³ however a planar conformation may also be imposed either by very bulky substituents or via intramolecular heteroatom-tellurium interactions.¹⁶² A possible source of the spirocyclic dianion **67** is the reaction of the dianion **64** ($\text{E} = \text{Te}$) with *in situ*-generated cyclic tritelluride **68**. The potentially versatile coordination behavior of the hard (N) and soft (Te) donor centers in **67** is illustrated by comparing the bis(N,N') coordination observed in the sodium derivative $[\text{Na}(\text{TMEDE})]_2\textbf{67}$ with the tridentate ($\text{Te}, \text{Te}', \text{Te}''$) bonding found in the rhodium(III) complex $\text{Cp}^*\text{Rh}\textbf{67}$.¹⁸⁷

Figure 31. Products of the oxidation of alkali-metal complexes of **64** (E = Te) with I₂.

7.6.3 p-Block Metal Complexes

The potential of the ditelluro dianion **64** (E = Te) for the incorporation of other p-block elements into phosphorus-tellurium ring systems has been previously indicated in Section 5.2 with the synthesis of organophosphorus(III)-tellurium via metathesis between RPCl_2 (R = Ad, ^tBu) and $[\text{Li}(\text{TMEDA})]_2\textbf{64}$ (E = Te) to give the RP-bridged derivatives **1** (Scheme 9b).¹⁴ Another example is the preparation of the cyclic tritelluride **68** by reaction of $[\text{Na}(\text{TMEDA})]_2\textbf{64}$ (E = Te) with $\text{TeCl}_2 \cdot \text{TMTU}$.¹⁸³ The results of a broader investigation of the metathetical reactions of $[\text{Li}(\text{TMEDA})]_2\textbf{63}$ with p-block element halides are depicted in Scheme 18.¹⁸⁸

In summary, those studies revealed that the dianion **64** (E = Te) engages in *Te,Te'*-chelation to the metal in Ph_2Ge (**69**) and R_2Sn (**70**, R = ^tBu, ⁿBu, Ph) derivatives. In the reaction with Se_2Cl_2 the products **71** and **72**, in which either one or two selenium atoms occupy the bridging positions, were characterized by a combination of multinuclear NMR spectroscopy and X-ray analysis.¹⁸⁸ The lability of the P–Te bond is evident, however, in reactions with group 13 trihalides MCl_3 (M = Ga, In), which generate the neutral spirocyclic complexes **73** (M = Ga, In) in which the loss of a Te atom leaves a terminal P^{III} center in one of the ligands.¹⁸⁸

Scheme 18. p-Block Element-Tellurium Heterocycles Supported by P_2N_2 Rings. Adapted from ref. 188. Copyright 2015 American Chemical Society.

8 SINGLE-SOURCE PRECURSORS FOR METAL TELLURIDE THIN FILMS

There is considerable current interest in the fabrication of thin films of metal tellurides, notably CdTe , Sb_2Te_3 , PbTe , and in their formation as quantum dots because of potential applications as low-band gap semiconducting materials in solar cells, thermoelectric devices, and telecommunications. In Section 6.7 examples of the use of phosphine tellurides, especially, tri-*n*-octylphosphine telluride, as a reactive source of tellurium for generating tellurides of group 11, 12 and 14 metals in the form of nanomaterials or quantum wires were presented. In this section the applications of metal complexes of telluroimidophosphinites (**42**) and ditelluroimidodiphosphinates (**45**) as *single-source* precursors for the generation of binary metal tellurides are discussed.

In the mid-1990s Bochmann and co-workers synthesized several homoleptic metal complexes of the type $\text{M}(\text{42})_2$ ($\text{R} = \text{tBu}$, $\text{R}' = \text{iPr}$, Cy ; $\text{M} = \text{Zn}$, Cd , Cr , Mn , Fe , Co) (Section

7.3.3).^{165,166} The thermolysis of the transition-metal complexes produced thin films of metal ditellurides MTe_2 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}$).¹⁶⁶ Thermally stable, sublimable group 12 complexes were shown to produce thin films of MTe ($\text{M} = \text{Zn}, \text{Cd}$) free from phosphorus contamination.^{189,190}

More recently, O'Brien and co-workers have carried out an extensive evaluation of the suitability of homoleptic complexes of **45** ($\text{R} = \text{iPr}$) with group 11, 12, 14 and 15 metals (Scheme 13), as well as the group 13 complex **57**, as single-source precursors for metal tellurides using the aerosol-assisted chemical vapor deposition (AACVD) technique.¹⁶ The results are summarized in Table 4. Under appropriate conditions the AACVD technique was successful for producing pure thin films of cubic CdTe from **50** ($\text{M} = \text{Cd}$), however a similar approach resulted in decomposition of the corresponding mercury complex **50** ($\text{M} = \text{Hg}$) to hexagonal tellurium.¹⁹¹ In a subsequent study the use of atmospheric pressure CVD generated CdTe in the form of epitaxial rods.¹⁹² The AACVD technique was also successful for the synthesis of rhombohedral Sb_2Te_3 in the form of hexagonal-shaped nanoplates¹⁹³ and phase-pure PbTe ¹⁷¹ from **51** ($\text{M} = \text{Sb}$) and **52** ($\text{M} = \text{Pb}$), respectively. By contrast, however, the congeners **51** ($\text{M} = \text{Bi}$) and **52** ($\text{M} = \text{Sn}$) produced only elemental tellurium.^{171,193} The coinage metal precursors **53**, **54** and **59** ($\text{R} = \text{iPr}$) generated a metal telluride admixed with tellurium (Table 4).¹⁷⁴ The formation of elemental tellurium presumably results from the high Te/M ratio in the precursors. However, the use of the homoleptic Hg^{II} complex of the *monotellurido* ligand **44**, $\text{Hg}(\text{TeP}^{\text{iPr}}\text{Pr}_2\text{N}^{\text{iPr}}\text{Pr}_2\text{P})_2$, did not produce pure HgTe .¹⁵⁸

The AACVD of the indium complex **57** provided the first report of the generation of pure cubic In_2Te_3 from a molecular precursor.¹⁹⁴ By contrast, the gallium analog **56** produced a mixture of Ga_2Te_3 , GaTe and tellurium.¹⁹⁴ The production of metal tellurides (and tellurium) from the AACVD of complexes of **45** presumably results from the lability of the $\text{P}-\text{Te}$ bond in the single-source precursors. In the specific case of **57**, some insight into the process that generates In_2Te_3 was gleaned from the electrospray mass spectrum (ESMS) of the precursor in THF, which displayed peaks attributable to the homoleptic cation $[\text{In}\{\text{N}(\text{P}^{\text{iPr}}\text{Pr}_2\text{Te})_2\}_2]^+$ and the fragment anion

$[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]^-$ in the form of the diprotonated species.¹⁹⁴ These observations suggest that the deposition of In_2Te_3 occurs directly from the central In_3Te_3 ring in **57**.

Complexes of the mixed chalcogen ligands $[\text{N}(\text{P}^i\text{Pr}_2\text{E})(\text{P}^i\text{Pr}_2\text{Te})]^-$ (E = S, Se) are potential single-source precursors of ternary metal chalcogenides that incorporate two different chalcogens. This possibility was investigated for the AACVD of the nickel(II) complex $\text{Ni}[\text{N}(\text{P}^i\text{Pr}_2\text{Se})(\text{P}^i\text{Pr}_2\text{Te})]$, but only NiTe_2 was generated.¹⁷⁷

Table 4. Metal Telluride Formation from Complexes of 45 (R = ^iPr)

Precursor	Metal Telluride Products	Ref.
50 (M = Cd)	Cubic CdTe	191
50 (M = Cd)	Epitaxial CdTe Rods	192
50 (M = Hg)	Hexagonal Te	191
51 (M = Sb)	Rhombohedral Sb_2Te_3	193
52 (M = Pb)	Cubic PbTe	171
53	Orthorhombic CuTe + Te	174
54	Hexagonal Plates of Ag_7Te_4 + Te	174
59 (R = ^iPr)	Monoclinic AuTe_2 + Te	174
56	Cubic Ga_2Te_3 , GaTe + Te	194
57	Cubic In_2Te_3	194

9. CONCLUSIONS AND PROSPECTS

Organophosphorus-tellurium chemistry has developed slowly over the past 65 years in comparison with the chemistry of sulfur and selenium analogues.¹⁻⁶ In part, this tardiness can be attributed to the thermal and photochemical lability of phosphorus-tellurium bonds that makes many of these compounds difficult to manipulate. Significantly, there is no tellurium counterpart of the Lawesson's or Woollins' reagents, which contain both bridging (P–E) and terminal P=E (E = S, Se, respectively) functionalities; the latter reagents find wide applications in organic chemistry for the conversion of C=O to C=E groups. On the other hand, there are numerous recent examples in which the lability of the P=Te bond in triorganophosphine tellurides has been employed creatively as a reactive source of tellurium(0) to generate binary metal tellurides in the form of quantum dots or nanomaterials with unusual properties for applications in *inter alia* IR detection, thermoelectric materials and solar cells (Section 6.7). Several recent studies have established that the introduction of a negative charge confers added stability on P–Te bonds (Sections 3 and 7) and the coordination chemistry of the resulting anions has been widely explored. In many cases the resulting metal complexes serve as efficient single-source precursors of pure main group or transition-metal tellurides in the form of thin films or quantum dots. The exploitation of the lability of the P–Te bond in the generation of semi-conductors with novel properties will continue to have an important impact in materials science.

NMR studies of phosphorus-tellurium compounds and, in particular, the magnitude of the one-bond coupling constant $^1J(^{31}\text{P}, ^{125}\text{Te})$ are of considerable interest. The value of this parameter can range from as low as 100 Hz in organophosphorus(III)-tellurium compounds (Table 1 and Section 5) to as high as 2290 Hz in organophosphorus(V)-tellurium compounds (Table 3 and Section 6.2). The anomalously high values in the range 1210-1360 Hz observed for weak (“through space”) P $\cdots$ Te interactions ($d(\text{P}\cdots\text{Te}) = 3.09\text{-}3.20 \text{ \AA}$) in *peri*-substituted compounds have been explained satisfactorily in terms of three-center four-electron interactions (Section 5.3). However,

the nature of phosphorus-tellurium bonding in both organophosphorus(III)- and organophosphorus(V)-tellurium systems awaits a modern theoretical treatment in order to determine the relative contributions of the factors that determine the disparate values of $^1J(^{31}\text{P}, ^{125}\text{Te})$ not only between organophosphorus(III) and organophosphorus(V) compounds, but also the large variations within those two series.

From a fundamental perspective, binary phosphorus-tellurium cations are reasonable synthetic targets in view of the recent report of the preparation of the intriguing phosphorus-selenium cation $[\text{P}_3\text{Se}_4]^+$ by three different routes,¹⁹⁵ two of which are applicable to P-Te systems. In a similar vein the characterization of the binary anionic species $[\text{P}_4\text{Te}_2]^{2-}$ (Section 3) suggests that similar P-Te anions may be generated by reactions of polyphosphides, e.g. P_7^{3-} and P_5^- , with tellurium. Finally, in terms of applications, the further exploitation of the labile nature of the P-Te bond combined with the oxophilicity of P^{III} centers in organic synthesis (Section 7.1) warrants further investigation in the light of recent results and the historical context provided in this review.

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Notes

The authors declare no competing financial interest.

Biographies

Tristram Chivers, a native of Bath, England, received his BSc, PhD and DSc degrees all from the University of Durham (UK). He joined the University of Calgary in 1969 and served as Head of the Chemistry Department from 1977 to 1982. He currently holds the title of Faculty Professor and Professor Emeritus of Chemistry. His primary research interests are in the general area of main group element chemistry with emphasis on chalcogen chemistry and inorganic ring systems. He is the author of two books: “A Guide to Chalcogen-Nitrogen Chemistry” and (with I. Manners) “Inorganic Rings and Polymers of the p-Block Elements: From Fundamentals to Applications”. He received the Alcan Lecture Award of the Canadian Society for Chemistry (CSC) in 1987, the Royal Society of Chemistry Award (UK) for Main-Group Element Chemistry in 1993, and the E.W.R. Steacie Award from the CSC in 2001. He was elected a Fellow of the Royal Society of Canada in 1991. He was awarded an honorary DSc from the University of Oulu, Finland in 2006. In 2008 he was the recipient of the ASTech Outstanding Leadership in Alberta Science Award.

J. Derek Woollins was born in Cleethorpes and educated at the University of East Anglia (Norwich), where he went on to carry out his PhD under the supervision of Andrew Thomson and Roger Grinter. He carried out postdoctoral work with Bill Cullen (UBC, Vancouver), Barnett Rosenberg (MSU, Michigan) and Norman Greenwood (Leeds, England) before being appointed as a lecturer at Imperial College London. After 12 years at Imperial College, he moved to Loughborough as the Chair in Inorganic Chemistry, where he stayed for 5 years

before moving to St Andrews as the Chair in Synthetic Chemistry in 1999. He is currently Vice Principal (Research) and Provost at St Andrews. Woollins has published over 500 research papers in main group chemistry and three books. His research interests center around group 15/16 chemistry including the use of P-Se compounds (such as Woollins' Reagent) in synthesis and structural science. He was elected to Fellowship of the Royal Society of Edinburgh in 2002, to the European Academy of Sciences in 2008 and to the European Academy of Science and Arts in 2012.

Andreas Nordheider was born and raised in Melle, Germany and received his degrees in Chemistry and Biochemistry (BSc) as well as his MSc in Chemistry from the Ludwig-Maximilians-University (LMU) Munich. He conducted research on heterocyclic nitrogen-rich explosives under the supervision of Prof. Thomas Klapötke and investigated niobium complexes and the activation of white phosphorus at the Massachusetts Institute of Technology under the guidance of Prof. C. Cummins. His PhD was completed 2014 at the University of St Andrews, Scotland working on "Phosphorus-Tellurium Heterocycles and Their Lighter Chalcogen Analogues – From Small Molecules to Macrocycles" in the group of Prof. J. Derek Woollins. As a part of his PhD he moved to the University of Calgary, Canada to work with Prof. Tristram Chivers focusing on P₂N₂-supported chalcogen systems. He received an EPSRC postdoctoral fellowship prize in 2014 and, subsequently, joined a Management Consulting Company, where he is a Consultant for Operational Excellence and Organizational Transformation.

ABBREVIATIONS

AACVD	aerosol-assisted chemical vapor deposition
Ad	adamantyl
Bbt	2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl
^t Bu ₂ Im	1,3-di- <i>tert</i> -butyl-imidazolin-2-ylidene
Bupp ₂ Ph ₄	(^t BuP(CH ₂ CH ₂ PPh ₂) ₂)
Ch	chalcogen
CIP	contact ion pair
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
Cp	cyclopentadienyl (C ₅ H ₅)

Cp*	pentamethylcyclopentadienyl (C ₅ Me ₅)
CVD	chemical vapor deposition
Cy	cyclohexyl
DFT	density functional theory
Dipp	diisopropylphenyl (2,6- ⁱ Pr ₂ C ₆ H ₃)
DME	dimethoxyethane
Dp	<i>meso</i> -Me ₂ Si(^t BuC ₅ H ₃) ₂
DPPE	1,2-bis(diphenylphosphino)ethane
DT	ditelluride
ESMS	electrospray mass spectrometry
Fc	ferrocenyl (Fe(C ₅ H ₅) ₂)
Fc*	2,5-bis(3,5-di- <i>t</i> -butylphenyl)ferrocenyl
FLP	frustrated Lewis pair
HOMO	highest occupied molecular orbital
IPr	(2,6-isopropylphenyl)imidazole-2-ylidene
L	ligand
LUMO	lowest unoccupied molecular orbital
Mes	mesityl (2,4,6-Me ₃ C ₆ H ₂)
Mes*	supermesityl (2,4,6- ^t Bu ₃ C ₆ H ₂)
Morp	morpholino
Ms ₂ N ⁻	di(methylsulfonyl)amide
Ms ₂ N ⁻	di(methylsulfonyl)amide
NMR	nuclear magnetic resonance
Pip	piperidino
Pyrr	pyrrolidino
SOMO	singly occupied molecular orbital
Tbt	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl {[2,4,6-(Me ₃ Si) ₂ CH] ₃ }C ₆ H ₂
Ter	2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-(2,4,6-Me ₃ C ₆ H ₂) ₂ C ₆ H ₃)
THF	tetrahydrofuran
TIP	2,4,6-triisopropylphenyl (2,4,6- ⁱ Pr ₃ C ₆ H ₂)
TMEDA	tetramethylethylenediamine
TMTU	tetramethylthiourea
TOP	tri- <i>n</i> -octylphosphine
TOPO	tri- <i>n</i> -octylphosphine oxide

TOPTe	tri-n-octylphosphine telluride
Trit	trityl (triphenylmethyl) (Ph_3C)
UV	ultra-violet

Dedication

This article is dedicated to Professor Ralph A. Zingaro and Professor Dr. Wolf-Walther du Mont in recognition of their seminal contributions to the development of organophosphorus(V)-tellurium and organophosphorus(III) – tellurium chemistry, respectively.

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