

Isolatable organophosphorus(III)-tellurium heterocycles

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A new structural arrangement $\text{Te}_3(\text{RP}^{\text{III}})_3$ and the first crystal structures of organophosphorus(III)-tellurium heterocycles are presented. The heterocycles can be stabilized and structurally characterized by (a) the appropriate choice of substituents in $\text{Te}_m(\text{P}^{\text{III}}\text{R})_n$ ($m = 1$: $n = 2$, $\text{R} = \text{OMes}^*$; $n = 3$, $\text{R} = \text{Ad}$; $n = 4$, $\text{R} = \text{Fc}$; $m = n = 3$: $\text{R} = \text{Trt}$, Mes^*) or (b) the installation of a $\text{P}^{\text{V}}_2\text{N}_2$ anchor in $\text{RP}^{\text{III}}[\text{TeP}^{\text{V}}(t\text{BuN})(\mu\text{-N}t\text{Bu})_2]$ ($\text{R} = \text{Ad}$, $t\text{Bu}$).

Keywords: heterocycles · NMR-spectroscopy · phosphorus · tellurium · X-ray diffraction

Introduction

Compounds such as Lawesson's reagent $[(4\text{-MeOC}_6\text{H}_4)\text{P}=\text{S}(\mu\text{-S})_2]$ (**LR**)¹ and Woollins' reagent $[\text{PhP}=\text{Se}(\mu\text{-Se})_2]$ (**WR**)² illustrate that organophosphorus-sulfur and -selenium compounds have been studied extensively not least because of their interesting reactivity towards organic compounds.^{3,4} In contrast, organophosphorus-tellurium heterocycles $(\text{RP})_n\text{Te}_m$ have been only sporadically investigated.⁵ The systems were usually obtained as mixtures and characterized by a combination of solution-state ³¹P and ¹²⁵Te NMR as well as mass spectrometry.⁶⁻⁹

The different synthetic approaches that were developed to generate organophosphorus(III)-tellurium heterocycles include reactions of

- RP-Si reagents [$\text{R} = t\text{Bu}$] with tellurium^{6,7}
- RPCl_2 [$\text{R} = t\text{Bu}$, $\text{R}'_2\text{N}$ ($\text{R}' = i\text{Pr}$, Cy , Ph)] with Na_2Te , Li_2Te_2 or $\text{Te}(\text{SiMe}_3)_2$ ⁶⁻⁹
- $t\text{Bu}(\text{Cl})\text{P-P}(\text{Cl})t\text{Bu}$ with Na_2Te ^{5,6} or
- $n\text{Bu}_3\text{P}\text{Te}$ with the diphosphene $\text{TbtP}=\text{PFc}$ ($\text{Tbt} = 2,4,6\text{-tris[bis(trimethylsilyl)methyl]-phenyl}$)¹⁰

These pathways produced a series of organophosphorus(III)-tellurium heterocycles with different structural arrangements, as depicted in Figure 1. So far, the findings regarding these systems by du Mont^{6,7}, Karaghiosoff^{8,9} and Tokitoh¹⁰ lead to the following conclusions:

- 3-, 4- and 5- membered rings containing one Te atom and 5- and 6-membered ring incorporating one $\text{Te-P}^{\text{III}}\text{-Te}$ unit and two $\text{P}^{\text{III}}\text{-Te-P}^{\text{III}}$ units, respectively, are possible (see Figure 1, left-hand and centre columns)

- stable heterocycles containing both terminal (*exo*) and bridging (*endo*) Te atoms, i.e. a $\text{P}=\text{Te}(\mu\text{-Te})$ unit, cf. **LR** and **WR**, are unlikely
- CF_3 substituents on P improve the stability of the rings with respect to loss of Te in solution, whereas NR_2 groups do not have the same stabilizing influence
- the pure 3- and 4-membered rings that were isolated $(t\text{BuP})_n\text{Te}$ ($n = 2,3$) are yellow or red liquids at RT
- the reported compounds are air-sensitive, some show light-sensitivity and thermal instability, which complicates the isolation and characterization
- no solid-state structures have been reported.

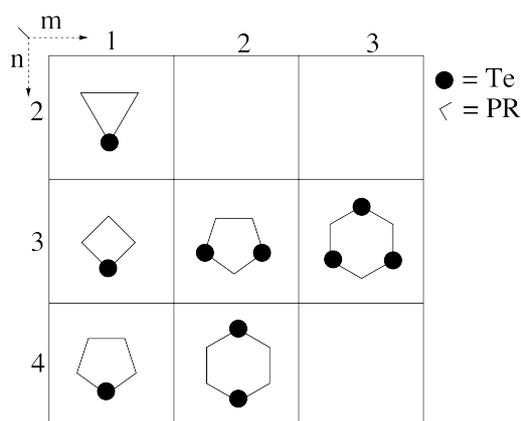


Figure 1. Structural arrangements of organophosphorus(III)-tellurium heterocycles $(\text{RP})_n\text{Te}_m$, including this work. The existence of $\text{Te}_2(\text{RP})_4$ is tentative based on limited NMR data.⁷

In this paper we describe two new synthetic approaches to organophosphorus(III)-tellurium heterocycles that have led to (a) the first examples of ring systems that incorporate an equal number of alternating P and Te atoms, i.e. $\text{Te}_3(\text{PR})_3$ ($\text{R} = \text{Mes}^*$, Trt ; $\text{Trt} = \text{trityl} = \text{-CPh}_3$), (b) the first solid-state structural characterizations of $\text{Te}_m(\text{RP})_n$ rings including $\text{Te}_3(\text{PR})_3$, $\text{Te}(\text{PR})_2$ ($\text{R} = \text{OMes}^*$), $\text{Te}(\text{PR})_3$ ($\text{R} = \text{Ad}$) $\text{Te}(\text{PR})_4$ ($\text{R} = \text{Fc}$), and (c) P_2N_2 -stabilized organophosphorus(III)-tellurium rings.

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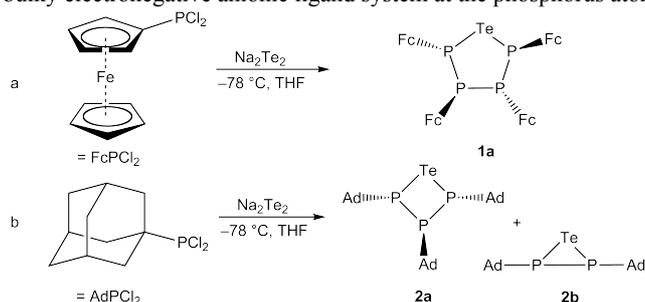
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Results and discussion

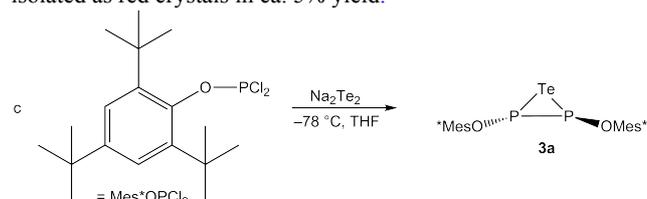
Synthesis and multinuclear NMR spectra of organophosphorus(III)-tellurium heterocycles

The first synthetic approach involves the reaction of RPCl_2 ($\text{R} = \text{Fc}$, Ad , Mes^*O , Mes^* , Trt) with Na_2Te_2 in THF (Scheme 1). These R groups were chosen since they provide significant steric bulk (Mes^* , Trt) and the Fc analogue of **LR** has proved to be very stable.¹¹ Furthermore, an adamantyl ligand at a phosphorus atom was shown to have similar reactivity and characteristics to the *tert*-butyl ligands. The reactions of the adamantyl-substituted compounds are usually slower but crystallization is favored in comparison to *tert*-butyl compounds.¹² The Mes^*O substituent was used as an example of a bulky electronegative anionic ligand system at the phosphorus atom.



Scheme 1. Reaction of (a) FcPCl_2 and (b) AdPCl_2 with Na_2Te_2 in THF.

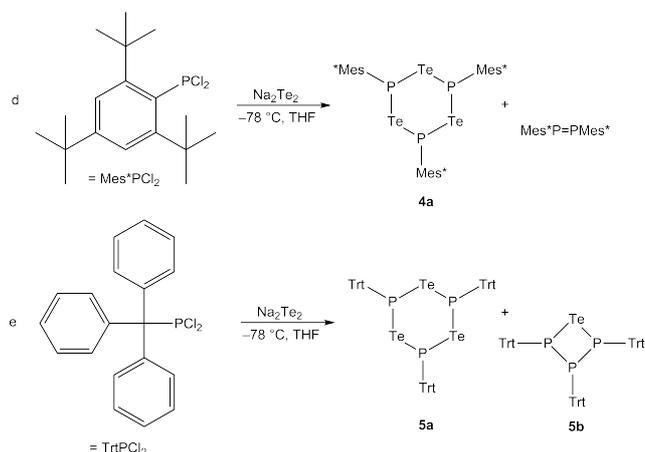
Treatment of FcPCl_2 with an equimolar amount of Na_2Te_2 in THF at $-78\text{ }^\circ\text{C}$ produced **1a** as the major product with the cyclopentaphosphane (FcP)₅ as a by-product, which was identified by X-Ray crystallography. The 2,3,4,5-tetra-ferrocenyl-1-tellura-2,3,4,5-tetraphospholane **1a** was isolated as an orange to red solid with low solubility, which can however be recrystallized from hot toluene to yield pure **1a** in low yield. By contrast, the reaction of AdPCl_2 with Na_2Te_2 under similar conditions yielded the telluradiphosphirane **2b** as the main product and the telluratetraphosphorane **2a** as a minor product (^{31}P NMR); **2a** was isolated as red crystals in ca. 5% yield.¹⁴



Scheme 2. Reaction of $\text{Mes}^*\text{OPCl}_2$ with Na_2Te_2 in THF.

Similarly $\text{Mes}^*\text{OPCl}_2$ was reacted with Na_2Te_2 to yield the telluradiphosphirane **3a**, which was isolated in a yield of 37 % after recrystallization from hexane.

Finally, the reaction of Mes^*PCl_2 and TrtPCl_2 with an equimolar amount of Na_2Te_2 gave rise to the novel tritelluratetraphosphorinanes **4a** (Mes^*PTe)₃ and **5a** (TrtPTe)₃, which were characterized by NMR spectroscopy. For the reaction with Mes^*PCl_2 the disphosphene ($\text{Mes}^*\text{P}=\text{PMes}^*$)¹⁵ was observed as a major by-product and together with elemental Te also as the decomposition product, when left in solution for more than 24 h. For the TrtPCl_2 reactions a telluratetraphosphorane **5b** was identified as a minor product besides other unknown compounds. In contrast to **1a**, **2a**, **2b** and **3a** these compounds (**4a**, **5a**, **5b**) are highly air sensitive and slightly light sensitive.



Scheme 3. Reaction of d) Mes^*PCl_2 and e) TrtPCl_2 with Na_2Te_2 in THF.

The ^{31}P NMR spectrum of **1a** exhibits a second order AA'MM' pattern (considering the ^{125}Te -containing isotopomer it expands to an AA'MM'X spin system). The characteristic values (shift and coupling constants) were calculated by iterative fitting as shown in Figure 2.

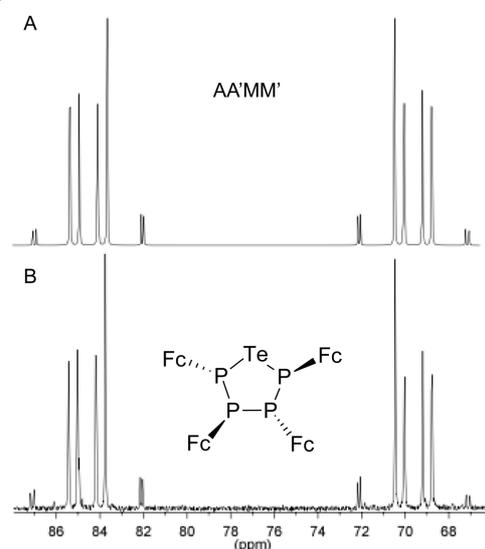


Figure 2. ^{31}P NMR spectrum (202.47 MHz) of **1a**: (A) AA'MM' spectrum calculated by iterative fitting, (B) experimental spectrum.¹⁶

The P1/P1' resonances appear at 84.5 ppm revealing a $^1J_{\text{P1-P2}}$ -coupling of -305.1 Hz, a $^2J_{\text{P1-P2}/\text{P1'-P2'-P2}}$ -coupling of 31.0 Hz and a $^2J_{\text{P1-P1'}}$ -coupling of 8.0 Hz. The P2/P2' resonances are observable at 69.6 ppm with a $^1J_{\text{P2-P2'}}$ -coupling of -339.0 Hz.¹⁷ The very poor solubility of **1a** precluded the observation of ^{125}Te satellites as well as characterization by ^{125}Te NMR.

The adamantyl derivative **2a** shows a first order A_2M -type ^{31}P NMR spectrum (considering the ^{125}Te -containing isotopomer it expands to an A_2MX -type spectrum), consistent with an all-*trans* orientation of the phosphorus substituents. The P2/P4 atoms appear as a doublet at -66.6 and the P3 atom as a triplet at -26.3 ppm. The $^1J_{\text{P-P}}$ coupling is 169.0 Hz; the $^1J_{\text{P-Te}}$ coupling was not observed, possibly due to its surprisingly very low value of <8 Hz. The ^{125}Te NMR spectrum of **2a** showed a doublet at -461.1 ppm ($^2J_{\text{P-Te}} = 80$ Hz). The ^{31}P NMR spectrum of **2b** consists of a singlet (A_2X spin system) at -79.8 ppm accompanied by a set of tellurium satellites (^{125}Te , $I = 1/2$, 7.1%), with $^1J_{\text{P-Te}} = 220.6$ Hz. In the ^{125}Te NMR spectrum one resonance at -818.3 ppm ($^1J_{\text{P-Te}} = 218.4$ Hz) is observed. The chemical shifts and coupling constants for **2a** and **2b** are in good agreement with the reported values of the corresponding *t*Bu-substituted derivatives, reported by du Mont et al.⁶

A single resonance at 78.5 ppm is observed in the ^{31}P NMR spectrum of **3a** (as in **2b** a A_2X spin system), which is shifted significantly to low field compared to **2b**, presumably due to the electronegativity of the Mes*O substituent. The tellurium satellites revealed a coupling constant $^1J_{\text{P-Te}}$ of 396.9 Hz which is quite high compared to **2b** or the reported derivatives by du Mont et al. (229 Hz),⁶ Tokitoh et al. (260 Hz)¹⁰ or Karaghiosoff et al. (285.2 Hz).⁹ The observations are consistent with the triplet resonance in the ^{125}Te NMR spectrum at 7.7 ppm, which also shows a significantly low field shift when compared to the other reported P_2Te -systems and **2b**.

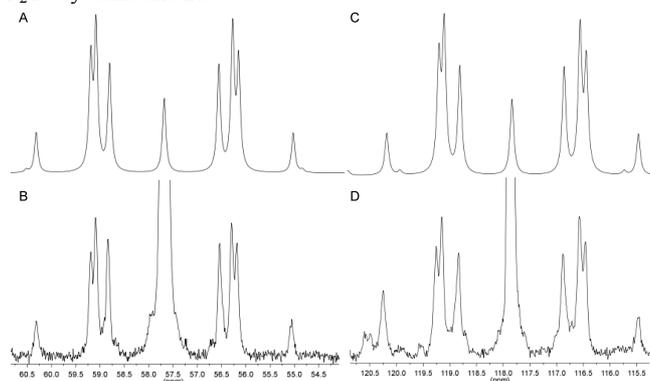


Figure 3. ^{31}P NMR spectra (109.37 MHz) of **4a** (AB) and **5a** (CD). (AC): A-parts of the $\text{A}_2\text{A}'\text{X}$ spectra calculated by iterative fitting, (BD): experimental spectra.

The ^{31}P NMR spectra of **4a** and **5a** display singlets at 57.7 ppm (**4a**) and 117.9 ppm (**5a**) with a characteristic pattern for the A-part of an $\text{A}_2\text{A}'\text{X}$ -spectrum, shown in Figure 3. The coupling constants were calculated by iterative fitting of the simulated spectra depicted in A, C of Figure 3. The $^1J_{\text{P-Te}}$ values are rather large with -441.7 Hz (**4a**) and -398.7 Hz (**5a**) respectively (negative signs are derived from iterative fitting). The $^2J_{\text{P-P}}$ values were shown to be 325.0 Hz (**4a**) and 257.1 Hz (**5a**), $^3J_{\text{P-Te}}$ could not be observed. The large $^2J_{\text{P-P}}$ value is presumably due to a correlating alignment of the free electron pairs at the phosphorus(III) atoms, which would be consistent with a chair-like conformation of the P_3Te_3 rings with the substituents on the phosphorus atoms in equatorial positions. This was confirmed by a single crystal X-Ray structure of **5a**. The ^{125}Te NMR spectra are multiplets at 774.2 ppm (**4a**) and 598.9 ppm (**5a**) consistent with the simulation of an $\text{A}_2\text{A}'\text{X}$ spin system (Figure 4).

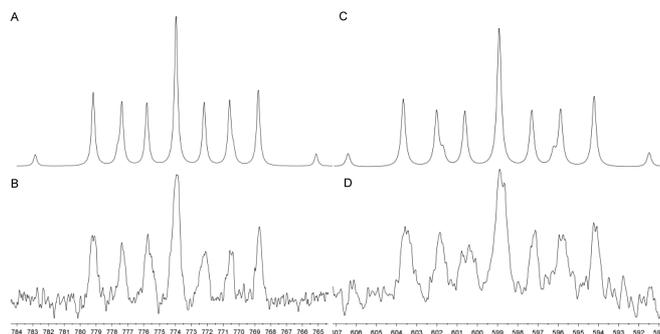


Figure 4. ^{125}Te NMR spectra (85.24 MHz) of **4a** (AB) and **5a** (CD). (AC): X-part of the $\text{A}_2\text{A}'\text{X}$ spectra calculated by iterative fitting, (BD): experimental spectra.

The ^{31}P NMR spectrum of telluratriphosphetane **5b** shows two resonances, a doublet at 131.8 ppm and a triplet at 82.1 ppm. In comparison to **2a** a small $^1J_{\text{P-Te}}$ coupling is visible at 72.2 Hz, in the form of satellites at the doublet. The $^1J_{\text{P-P}}$ value of 187.0 Hz is slightly larger than for **2a** (169.0 Hz) or the *t*Bu substituted derivative (172.6 Hz)⁶ but smaller than those with CF_3 substituents (248.7 Hz).⁹

X-ray structures of organophosphorus(III)-tellurium heterocycles

Crystals of 2,3,4,5-tetra-ferrocenyl-1-tellura-2,3,4,5-tetra-phospholane **1a** were isolated from toluene at -40 °C as red prisms. The crystal structure of **1a** (Figure 5) reveals that the P_4Te ring is non-planar with ferrocenyl groups alternating above and below the plane of the ring (all-*trans* conformation). The P–Te bond length of 2.503(6) Å is significantly shorter than the value of 2.565 Å reported for the $\text{P}^{\text{III}}\text{-Te}$ single bond in the acyclic compound $\text{Te}(\text{PiPr})_2$ ¹⁸, but similar to that found for a cyclic tritelluride anchored by $\text{P}^{\text{V}}_2\text{N}_2$ rings ($d(\text{P-Te}) = 2.532\text{-}2.540(1)$ Å).¹⁹ The P–P bond lengths of 2.188(8) Å and 2.163(8) Å are slightly shorter than those in the related *cyclo*-pentaphosphane (FcP)₅.¹³

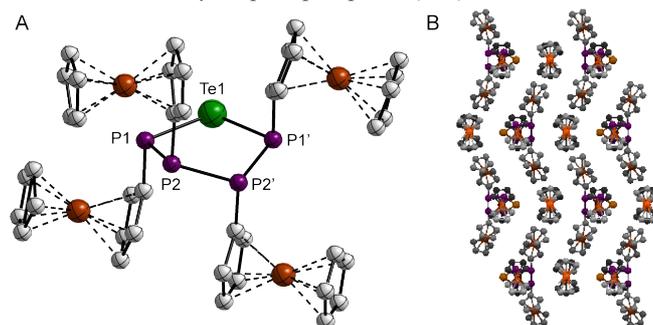


Figure 5. A: X-ray crystal structure of **1a**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–P1 2.503(6), P1–P2 2.188(8), P2–P2' 2.163(8), P1–C1 1.84(3), P2–C11 1.83(3); P1–Te1–P1 104.89(19), Te1–P1–P2 100.9(3), Te1–P1–C1 94.7(7), P1–P2–P2' 111.2(3), P2–P1–C1 99.4(7), P2'–P2–C11 103.5(7). B: packing along the *a*-axis.

Single crystals of 2,3,4-tris-adamantyl-1-tellura-2,3,4-triphosphetane **2a** were isolated from THF after storing the decanted reaction mixture at -40 °C for about two weeks (Figure 6). Two independent molecules with similar structural parameters are present in the unit cell ($Z = 8$). The P–Te bond lengths of 2.502(2) to 2.516(2) Å are close to that found for **1a**. However, the P–P bond lengths in **2a** are slightly longer than those in the corresponding *cyclo*-tetraphosphane (AdP)₄ [$d(\text{P-P})$ 2.2417(15)–2.2423(15) Å].²⁰ The four-membered P_3Te -Ring is non-planar and the adamantyl ligands adopt an all-*trans* conformation (Figure 6). The ring shows a torsion angle of 161.6°, cf. 151.7° in (AdP)₄.²⁰

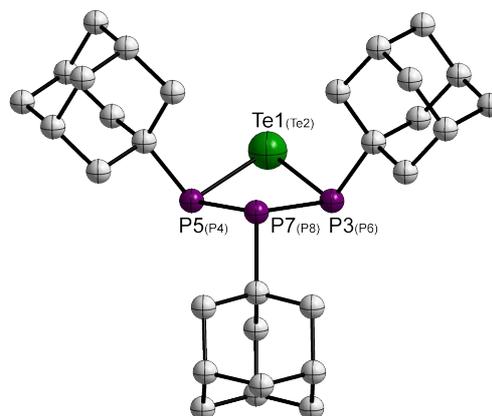


Figure 6. X-ray crystal structure of **2a**. H atoms omitted for clarity. Two distinct molecules within the unit cell (numbering scheme for the second independent molecule in parentheses): Selected bond lengths (Å) and angles (°): Te1–P3 2.502(2), Te1–P5 2.516(2), Te2–P4 2.507(2), Te2–P6 2.509(2), P3–P7 2.224(3), P4–P8 2.224(3), P5–P7 2.226(3), P6–P8 2.227(3), P3–C41 1.867(8), P4–C11 1.873(8), P5–C31 1.874(8), P6–C21 1.874(8), P7–C55 1.881(8), P8–C1 1.878(8); P3–Te1–P5 80.23(7), P4–Te2–P6 80.65(7), P7–P3–Te1 90.12(9), P8–P6–Te2 89.50(9), P7–P5–Te1 89.71(9), P8–P4–Te2 89.59(9), P3–P7–P5 93.19(11), P4–P8–P6 93.64(11).

The P–P–P-angle is at 93.19(12)° the largest endocyclic angle and also demonstrates the distortion as a consequence of the Te incorporation when compared to the tetrakis-adamantyl-*cyclo*-tetraphosphane (P–P–P 85.58(6)-87.10(6)°). The P–Te–P-angle is 80° and thus the smallest angle within the ring system. As for **1a**, no intermolecular Te⋯Te interactions are observed.

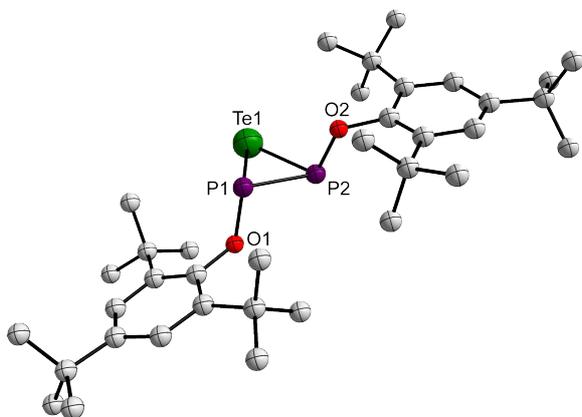


Figure 7. X-ray crystal structure of **3a**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–P1 2.4794(9), Te1–P2 2.4629(10), P1–P2 2.2473(10), P1–O1 1.6639(15), P2–O2 1.6675(17); P1–Te1–P2 54.09(3), Te1–P1–P2 62.58(3), Te1–P2–P1 63.33(3), Te1–P1–O1 107.54(6), P2–P1–O1 101.36(6), Te1–P2–O2 106.42(7), P1–P2–O2 102.28(7).

Yellow crystals of **3a** were isolated from a recrystallization using hexane at –40 °C. The X-Ray structure shown in Figure 7 reveals a three membered P₂Te ring system with comparatively short P–Te distances of 2.4629(10)-2.4794(9) Å and a slightly longer P–P distances than observed in **1a** and **2a**. The smallest angle within the ring system is as in **2a** the P–Te–P angle at 54.09(3)°. The Mes*O ligands on the phosphorus are in a *trans* position revealing a O–P–P–O torsion angle of 153.61°.

Excitingly, a recrystallization of **5a** from THF yielded orange prisms of the first tritelluratriphosphorinane suitable for single crystal X-Ray analyses. The structure and selected parameters are depicted in Figure 8.

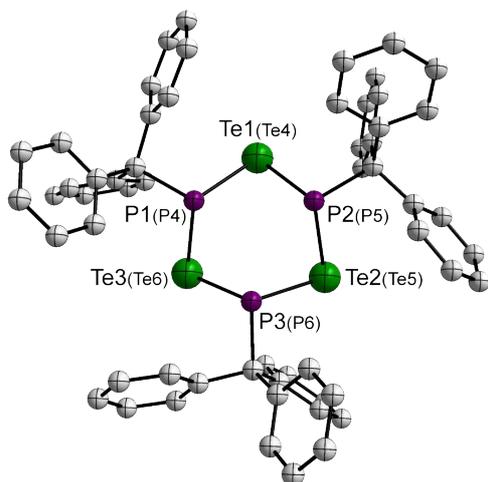


Figure 8. X-ray crystal structure of **5a**. H atoms and solvent molecules (four per P₃Te₃ system, eight per unit cell) omitted for clarity. Two distinct molecules within the unit cell (numbering scheme for the second independent molecule in parentheses): Selected bond lengths (Å) and angles (°): Te1–P1 2.502(3), Te1–P2 2.488(3), Te2–P2 2.508(3), Te2–P3 2.474(3), Te3–P1 2.482(3), Te3–P3 2.491(3), Te4–P4 2.482(3), Te4–P5 2.476(4), Te5–P5 2.492(4), Te5–P6 2.492(3), Te6–P4 2.498(3), Te6–P6 2.517(4), P–C 1.917(10)-1.938(12); P1–Te1–P2 83.41(9), P2–Te2–P3 82.52(9), P1–Te3–P3 80.94(9), P4–Te4–P5 81.80(10), P5–Te5–P6 82.51(10), P4–Te6–P6 81.70(10), Te1–P1–Te3 103.02(11), Te1–P2–Te2 104.45(11), Te2–P3–Te3 105.48(11), Te4–P4–Te6 105.67(11), Te4–P5–Te5 102.15(12), Te5–P6–Te6 102.10(12), Te–P–C 101.0(4)-105.6(4).

Two distinct molecules as well as eight THF solvent molecules are present in the unit cell. The P₃Te₃ ring crystallizes in the chair conformation, where the bulky trityl ligands are able to take the

sterically advantageous equatorial positions as shown in Figure 9 A. The only structure of a heavier chalcogen P^{III}₃Ch₃ system in the literature is a P₃S₃ ring reported by Goldwhite et al.,²¹ P₃Se₃ rings are unknown in the literature. The P₃S₃ system adopts a chair conformation in contrast to the few examples of P^{III}₃O₃ systems.²² The P–Te bond length of **5a** range from 2.474(3) to 2.517(4) Å, similar to those in the structures of **1a**, **2a** and **3a**. The P–Te–P angles are between 80.94(9) and 82.52(9)° and thus significantly smaller than the Te–P–Te angles (102.10(12)-105.67(1)°).

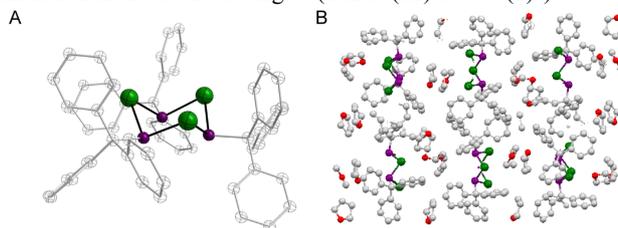
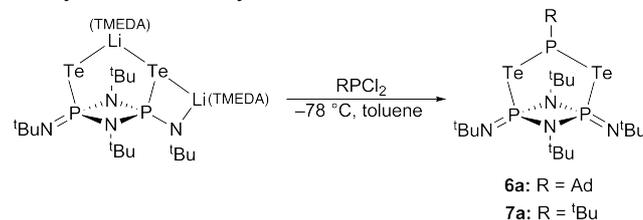


Figure 9. A) X-ray crystal structure of **5a** showing the chair-like conformation and B) packing of **5a** along the *a*-axis including the THF molecules (eight per unit cell). purple = P, green = Te, red = O

The packing along the *a*-axis is depicted in Figure 9 B, showing that the sterically demanding trityl substituents shield the P₃Te₃ rings from each other so that no interactions between the phosphorus(III)-tellurium rings are possible.

Synthesis, NMR spectra and X-ray structures of P₂N₂-stabilised organophosphorus(III)-tellurium heterocycles

The second synthetic pathway to organophosphorus-tellurium heterocycles utilises the reaction of R₂PCl₂ (R = Ad, *t*Bu) with [Li(TMEDA)]₂[*t*BuN(Te)P(μ-*Nt*Bu)₂P(Te)*Nt*Bu)]²³ (Scheme 4), a dianionic reagent that has proved to be effective in the preparation of a cyclic tritelluride by metathesis with TeCl₂·TMTU.¹⁹



Scheme 4. Reaction of [Li(TMEDA)]₂[*t*BuN(Te)P(μ-*Nt*Bu)₂P(Te)*Nt*Bu)] with AdPCl₂ and *t*BuPCl₂ in toluene.

The reactions of R₂PCl₂ (R = Ad, *t*Bu) with [Li(TMEDA)]₂[*t*BuN(Te)P(μ-*Nt*Bu)₂P(Te)*Nt*Bu)] in toluene at –78 °C produced **6a** as orange platelets and **7a** as orange prisms, respectively, which were identified by multinuclear NMR spectroscopy and mass spectrometry, elemental analyses and single-crystal X-Ray analyses.

The ³¹P NMR spectra of **6a** and **7a** are both characterized by a A₂M spin system (with the ¹²⁵Te-containing isotopomer it expands to an AA'MX type spectrum, where the isochronous P1 and P1' nuclei become magnetically inequivalent), showing a triplet at 89.5 (**6a**), 93.9 ppm, (**7a**) and a doublet at –129.0 (**6a**), –129.6 ppm (**7a**). Interestingly, the one-bond P–Te coupling constants involving P2 and P1 differ remarkably, ¹J_{P2–Te} = 420 (**6a**), 418 Hz (**7a**) and ¹J_{P1–Te} = 1073 (**6a**), 1073 Hz (**7a**) despite the close similarity in P–Te bond lengths (*vide infra*). The disparity in ¹J values is likely attributable to the difference in formal oxidation states of the two phosphorus atoms; the low value for the former is consistent with those found for P^{III}–Te compounds in this (*vide supra*) and previous work^{6, 8, 9, 24} whereas values > 1,000 Hz are observed for ditelluro derivatives of the P^V₂N₂ ring.^{19, 23, 25} The ¹²⁵Te NMR spectra displayed a doublet of

doublets pattern centered at 368.5 (**6a**), 423.4 ppm (**7a**) with $^1J_{P-Te}$ values that corroborate those found in the ^{31}P NMR spectra. The molecular structure of **6a** (Figure 9) contains a Te–P^{III}–Te unit bridging a P^V₂N₂ ring cf. the derivatives 1,3-Te₂(PR)₃ (R = *t*Bu, CF₃), which have been tentatively identified by NMR spectroscopy.^{7,9}

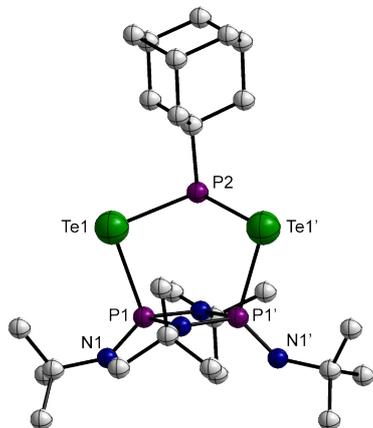


Figure 10. X-ray crystal structure of **6a**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–P1 2.512(3), Te1–P2 2.508(3), P1–N1 1.503(9), P1–N2 1.689(7), P1–N3 1.701(8), P2–C11 1.897(6); P1–Te1–P2 91.51(10), Te1–P1–N1 118.5(4), Te1–P1–N2 103.9(4), Te1–P1–N3 105.0(5), Te1–P2–Te1' 108.81(16), P1–N2–P1' 96.5(5), P1–N3–P1' 95.6(6).

The P–Te bond lengths [$d(P1-Te1) = 2.512(3)$ Å; $d(P2-Te1) = 2.508(3)$ Å] are equal within experimental error, despite the difference in oxidation states of these phosphorus atoms. The X-ray structure of **7a**²⁶ although disordered showed similar features to those described for **6a**.

Conclusions

In summary, the heterocycles **1a**, **2a**, **3a**, **5a**, **6a** and **7a** represent the first structurally characterized organophosphorus(III)-tellurium heterocycles. The reasonable thermal, air and light stability of these ring systems will facilitate investigations of their reactivity and coordination chemistry. In particular, the ligand behaviour of **1a**, **2a**, **3a** and **5a** can now be compared with the very limited information on metal complexes of Te(PR₂)₂.²⁷ From another perspective, the two Te and one P^{III} donor atoms in **6a** and **7a** offer the possibility of different coordination modes compared to **1a**, **2a**, **3a** and **5a**. Compounds **4a** and **5a** are the first representatives of heterocycles of the type Te_m(PR)_n ($m = n$) with an equal number of alternating phosphorus and tellurium atoms. Their thermal, air and light stability are significantly lower than those of the phosphorus-rich ring systems Te_m(PR)_n where $n > m$. Although Na₂Te₂ was found to be the most effective source of tellurium in salt-elimination reactions, it is notable that no P–Te heterocycles containing a –Te–Te– linkage were isolated or detected in solution (by NMR).

Experimental section

All synthetic manipulations were performed under an atmosphere of dry argon using standard Schlenk-line techniques and/or a *Saffron* glovebox running with argon unless otherwise stated. All glass apparatus were stored in a drying oven (120 °C) and flame dried in vacuo (10⁻³ mbar) before use. Dry solvents were collected from an MBraun solvent system under a nitrogen atmosphere and stored in Schlenk flasks over 4 Å molecular sieves. All chemicals were purchased from *Sigma Aldrich*, *ABCR*, *Acros Organics* and *Strem Chemicals Inc.* as long as not otherwise stated. Solution ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹²⁵Te{¹H} NMR spectra were recorded using a *JEOL DELTA EX 270*, a *BRUKER Avance II 400* or a *BRUKER Avance III 500* spectrometer. ¹H and

¹³C{¹H} NMR were referenced to TMS as internal standard, 85% H₃PO₄ was used as an external standard for ³¹P{¹H} NMR and Ph₂Te for ¹²⁵Te{¹H} NMR spectra, all NMR data was collected at 25 °C. Mass spectrometry was performed on a *MICROMASS LCT (ES)* and *MICROMASS GCT (EI, CI)* device. Elemental analysis was performed by a *CARBO ERBA CHNS* analyser as long as the compounds were stable enough at RT for measurements. Melting or decomposition points were determined by sealing the sample in capillaries and heating using a *Stuart SMP 30* melting point apparatus.

1a (FcP)₄Te: In a 100 mL Schlenk flask Na₂Te₂²⁸ (525 mg, 1.7 mmol) was suspended in dry THF (10 mL). The suspension was cooled down to –78 °C. A solution of FcPCl₂ (500 mg, 1.7 mmol) in dry THF (10 mL), also maintained at –78 °C, was added dropwise (5 min) by cannula with stirring. Stirring was continued for 3 h at that temperature and then at 20 °C for another 20 h. The reaction mixture was centrifuged and the clear yellow solution was decanted and stored for 3 days at –20 °C under an argon atmosphere until a green precipitate was formed. The solid product was removed by filtration and washed with THF. The residue was heated in boiling toluene for 2 h, and the solution was filtered hot (to remove (FcP)₅) and stored at –20 °C overnight to yield 2,3,4,5-tetra-ferrocenyl-1-tellura-2,3,4,5-tetraphospholane as red crystals (yield: 9 %). ³¹P NMR ([D₈]THF): δ = 84.5 (m, ¹J(P₁,P₂) = –305.1 Hz; ²J(P₁,P₂/P₁',P₂') = 31.0 Hz, ²J(P₁,P₁') = 12.0 Hz), 69.6 (m, ¹J(P₁,P₂) = –305.1 Hz; ¹J(P₂,P₂) = –339.0 Hz, ²J(P₁,P₂/P₁',P₂') = 31.0 Hz) ppm. ¹²⁵Te NMR ([D₈]THF): δ = no sharp signals due to low solubility. M.p. >200 °C. MS [Cl⁺, *m/z*], 992.9 [M+H]⁺ (calculated: 992.8 [M+H]⁺); HR-MS [APCI(ASAP, *m/z*), 994.8303 [M+H]⁺ (calculated: 994.8304 [M+H]⁺); EA calcd (%) for C₄₀H₃₆P₄TeFe₄: C 48.45, H 3.66, found: C 48.35, H 3.73.

2a (AdP)₃Te and **2b** (AdP)₂Te: Procedure as for **1a** using AdPCl₂²⁹ (500 mg, 2.1 mmol) and Na₂Te₂ (633 mg, 2.1 mmol). After the clear red solution had been decanted it was concentrated and stored at –40 °C. After 14 days crystals of **2a** appeared, which were filtered off and dried under vacuum (yield: <5%). The solvent was removed from the filtrate and the solid material washed with cold pentane to give **2b** (yield 36%).

2a: ³¹P NMR ([D₈]THF): δ = –66.6 (¹J(P,P) = 166.7 Hz), –26.3 (¹J(P,P) = 166.7 Hz) ppm. ¹²⁵Te NMR ([D₈]THF): δ = –461.1 (¹J(P,Te) = <8 Hz, ²J(P,Te) = 80 Hz) ppm. MS (EI⁺, *m/z*), 628.2 [M]⁺ (calculated: 628.2 [M]⁺). HR-MS (EI⁺, *m/z*) 620.1752 [M]⁺ (calculated: 620.1759 [M]⁺ = C₃₀H₄₅P₃¹²²Te₁). **2b**: ³¹P NMR ([D₈]THF): δ = –79.8 (s, ¹J(P,Te) = 220.6 Hz) ppm. ¹²⁵Te NMR ([D₈]THF): δ = –818.3 (s, ¹J(P,Te) = 218.4 Hz) ppm. M.p. >114 °C (dec). MS (EI⁺, *m/z*), 462.0 [M]⁺ (calculated: 462.1 [M]⁺).

3a (Mes*OP)₂Te: Procedure as for **1a** using Mes*OPCl₂³⁰ (500 mg, 1.4 mmol) and Na₂Te₂ (415 mg, 1.4 mmol). After the 20 h of stirring at RT the THF was removed and 25 mL of hexane added. The suspension was stirred for 30 min, filtered and the filtrate concentrated to about 8 mL. The yellow solution was stored at –40 °C, to afford yellow crystals after three days. The crystals were filtered off and dried under vacuum, the filtrate again concentrated and left at –40 °C for a second batch of crystals. The yellow material was dried under vacuum for 3 h resulting in an overall yield of 37 %.

¹H NMR ([D₈]THF): δ = 7.31 (s, 2H), 1.50 (s, 18H), 1.33 (s, 9H) ppm. ³¹P NMR ([D₈]THF): δ = 78.5 (s, ¹J(P,¹²⁵Te) = 396.9 Hz, ¹J(P,¹²³Te) = 332.1 Hz) ppm. ¹²⁵Te NMR ([D₈]THF): δ = 7.7 (t, ¹J(P,¹²⁵Te) = 394.6 Hz) ppm. M.p. >126 °C (dec). MS (EI⁺, *m/z*), 453.0 [M–OMes*]⁺ (calculated: 453.1 [M–OMes*]⁺); 601.1 [M–2*t*Bu+H]⁺ (calculated: 601.2 [M–2*t*Bu+H]⁺); 262.2 [OMes*+H]⁺ (calculated: 262.2 [OMes*+H]⁺); EA calcd (%) for C₃₆H₅₈O₂P₂Te: C 60.69, H 8.21, found: C 60.72, H 8.13.

4a (Mes*P)₃Te₃: Procedure as for **1a** using Mes*PCl₂³¹ (500 mg, 1.4 mmol) and Na₂Te₂ (434 mg, 1.4 mmol). After the clear yellow solution had been decanted the solvent was removed. The mixture was dissolved in hexane and filtered, followed by a removal of the hexane. The analysed mixture mainly contains Mes*P=PMes* (55%) and **4a** (40%). A recrystallization from hexane afforded orange crystals of Mes*P=PMes*, the main decomposition product of **4a**.

³¹P NMR ([D₈]THF): δ = 57.7 (s, ¹J(P,¹²⁵Te) = –441.7, ²J(P,P) = 325.0 Hz). ¹²⁵Te NMR ([D₈]THF): δ = 774.2 (m, ¹J(P,¹²⁵Te) = 442.0 Hz) ppm. MS (EI⁺, *m/z*): only fragments observed: 277.1 [PMes*+H]⁺ (calculated: 277.2 [M]⁺).

5a (TrtP)₃Te₃ and **5b** (TrtP)₂Te: Procedure as for **1a** using TrtPCl₂³² (500 mg, 1.5 mmol) and Na₂Te₂ (436 mg, 1.5 mmol). After the clear red solution had been decanted the solvent was removed. Recrystallization from THF at –40 °C afforded orange crystals of (TrtP)₃Te₃ in an overall yield of 8 %.

5a: ³¹P NMR ([D₈]THF): δ = 117.9 (s, ¹J(P,¹²⁵Te) = –398.7, ²J(P,P) = 257.1 Hz). ¹²⁵Te NMR ([D₈]THF): δ = 598.9 (m, ¹J(P,¹²⁵Te) 396.3 Hz) ppm. MS (EI⁺, *m/z*): only fragments observed: 243.1 [Trt]⁺ (calculated: 243.1 [Trt]⁺), Te_n ($n = 2, 3, 4, 5, 6$). EA calcd (%) for C₇₃H₇₇O₄P₃Te₃ (**5a** + 4 THF): C 58.69, H 5.19, found: C 58.51, H 4.98.

5b: ³¹P NMR ([D₈]THF): δ = 131.8 (d, ¹J(P,¹²⁵Te) = 72.2 Hz, ¹J(P,P) = 189.2 Hz, ²J(P,P) = 3.3 Hz), 82.1 (t, ¹J(P,P) = 187.0 Hz) ppm. ¹²⁵Te NMR ([D₈]THF): due to the low yield of **5b** no clear ¹²⁵Te resonance was observed; MS (EI⁺, *m/z*): see **5a**.

6a [(*t*Bu)P(μ-*N*'Bu)₂P(*N*'Bu)(μ-Te–P(Ad)–Te)]:

[Li(TMEDA)]₂[*t*BuN(Te)P(μ-*N*'Bu)₂P(Te)*N*'Bu] (500 mg, 0.59 mmol) was suspended in toluene (10 mL) and cooled to –78 °C. AdPCl₂ (140 mg, 0.59 mmol) was dissolved in toluene (10 mL), maintained at –78 °C and then added dropwise to the solution of [Li(TMEDA)]₂[*t*BuN(Te)P(μ-*N*'Bu)₂P(Te)*N*'Bu] over 15 min by cannula. The reaction mixture was stirred at that temperature for 2 h and then warmed to room temperature. After stirring for an additional 1 h, the precipitate (LiCl) was filtered off and the solvent

removed under vacuum. The obtained solid was dissolved in hexane and maintained at $-40\text{ }^{\circ}\text{C}$ overnight. The deep red crystals were filtered off and dried under vacuum. The resulting filtrate was concentrated and again placed in the freezer overnight to produce another batch of crystals (overall yield: 23 %). $^1\text{H NMR}$ (C_6D_6): $\delta = 1.98$ (m, 9H, Ad) 1.82 (s, 9H, ^tBu), 1.73 (s, 9H, ^iBu), 1.47 (s, 18H, ^iBu), 1.42 (m, 6H, Ad) ppm. $^{31}\text{P NMR}$ (C_6D_6): $\delta = 89.5$ (t, $^1J(\text{P,Te}) = 420$ Hz, $^2J(\text{P,P}) = 8.1$ Hz), -129.0 (d, $^1J(\text{P}_1,\text{Te}) = 1073$ Hz, $^2J(\text{P}_1,\text{P}_2) = 8.1$ Hz, $^2J(\text{P}_1,\text{P}_1') = 21$ Hz) ppm. $^{125}\text{Te NMR}$ ($[\text{D}_8]\text{toluene}$): $\delta = 368.5$ ($^1J(\text{P}_2,\text{Te}) = 418$ Hz, $^1J(\text{P}_1,\text{Te}) = 1073$ Hz, $^3J(\text{P,Te}) = 29$ Hz) ppm. MS (Cl^- , m/z), 769.1 [$\text{M}+\text{H}^+$] (calculated: 769.1 [$\text{M}+\text{H}^+$]); EA calcd (%) for $\text{C}_{26}\text{H}_{51}\text{N}_4\text{P}_3\text{Te}_2$: C 40.67, H 6.69, N 7.30, found: C 40.76, H 6.71, N 7.38.

7a [$(^t\text{BuN})\text{P}(\mu\text{-N}^i\text{Bu})_2\text{P}(\text{N}^i\text{Bu})(\mu\text{-Te-P}(^i\text{Bu})\text{-Te})$]:

Procedure as for **6a** using $^t\text{BuPCL}_2$ (94 mg, 0.59 mmol) and $[\text{Li}(\text{TMEDA})_2][^t\text{BuN}(\text{Te})\text{P}(\mu\text{-N}^i\text{Bu})_2\text{P}(\text{Te})\text{N}^i\text{Bu}]$ (500 mg, 0.59 mmol) (Yield: 18 %). $^1\text{H NMR}$ ($[\text{D}_8]\text{toluene}$): $\delta = 1.86$ (s, 9H, ^iBu), 1.72 (s, 9H, ^tBu), 1.45 (s, 18H, ^iBu), 1.40 (d, 9H, P^iBu), $^2J(\text{P,H}) = 12$ Hz) ppm. $^{31}\text{P NMR}$ ($[\text{D}_8]\text{toluene}$): $\delta = 93.9$ (t, $^1J(\text{P,Te}) = 418$ Hz, $^2J(\text{P}_2,\text{P}_1) = 8.1$ Hz), -129.6 (d, $^1J(\text{P,Te}) = 1073$ Hz, $^2J(\text{P}_1,\text{P}_2) = 8.4$ Hz, $^2J(\text{P}_1,\text{P}_1') = 21$ Hz) ppm. $^{125}\text{Te NMR}$ ($[\text{D}_8]\text{toluene}$): $\delta = 423.4$ ($^1J(\text{P}_2,\text{Te}) = 416$ Hz, $^1J(\text{P}_1,\text{Te}) = 1073$ Hz, $^3J(\text{P,Te}) = 32$ Hz) ppm. MS (Cl^- , m/z), 691.1 [$\text{M}+\text{H}^+$] (calculated: 691.1 [$\text{M}+\text{H}^+$]); EA: calcd (%) for $\text{C}_{20}\text{H}_{45}\text{N}_4\text{P}_3\text{Te}_2$: C 34.83, H 6.58, N 8.12, found: C 34.84, H 6.61, N 7.97.

X-ray crystal data for compounds **1a**, **3a**, **5a**, **6a** and **7a** were collected by a *Rigaku Mo MM007* (dual port) high brilliance generator with Saturn 70 and Mercury CCD detectors, rotating anode/confocal optics and two XStream LT accessories at $-180(1)\text{ }^{\circ}\text{C}$. **2a** was measured on a Nonius-KappaCCD, equipped with rotating anode at $-73\text{ }^{\circ}\text{C}$. All data were collected with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) and corrected for Lorentz and polarization effects.

These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. CCDC nos **1a** 945396, **2a** 945397, **3a** 961072, **5a** 961073, **6a** 945398, **7a** 945400, (**AdP**)₄945399.

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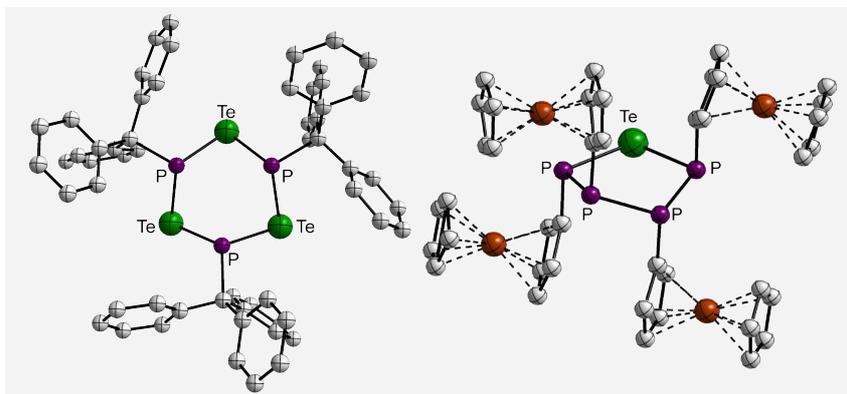
Layout 2:

Isolatable organophosphorus(III)- tellurium heterocycles

*Andreas Nordheider, Tristram Chivers, Oliver Schön, Konstantin Karaghiosoff, Kasun S Athukorala Arachchige, Alexandra M. Z. Slawin and J. Derek Woollins**

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Isolatable organophosphorus(III)- tellurium heterocycles



Organophosphorus(III)-tellurium heterocycles can be stabilized and structurally characterized by (a) the appropriate choice of substituents in $\text{Te}_m(\text{P}^{\text{III}}\text{R})_n$ ($m = 1$: $n = 2$, $\text{R} = \text{OMes}^*$; $n = 3$, $\text{R} = \text{Ad}$; $n = 4$, $\text{R} = \text{Fc}$; $m = n = 3$: $\text{R} = \text{Trt}$, Mes^*)

or (b) the installation of a $\text{P}^{\text{V}}_2\text{N}_2$ anchor in $\text{RP}^{\text{III}}[\text{TeP}^{\text{V}}(t\text{BuN})(\mu\text{-N}t\text{Bu})_2]$ ($\text{R} = \text{Ad}$, $t\text{Bu}$).