Isolatable organophosphorus(III)-tellurium heterocycles

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A new structural arrangement Te$_3$(RP)$_n$, 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 Te$_n$(RP)$_m$ ($m = 1$; n = 2, R = OMe*$; n = 3, R = Ad; n = 4, R = Fc; m = n = 3: R = Trt, Mes*) or (b) the installation of a P$_2$N$_2$ anchor in RP$_3$(tBuN)(µ-NiBu)$_2$ (R = Ad, tBu).

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

Introduction

Compounds such as Lawesson’s reagent [(4-MeOC$_2$H$_5$)$_2$P=S=Si(µ-S)]$_2$ (LR)$^7$ and Woollins’ reagent [PhP=Se(µ-Se)]$_2$ (WR)$^8$ illustrate that organophosphorus-sulfur and -selenium compounds have been studied extensively not least because of their interesting reactivity towards organic compounds.$^{8,14}$ In contrast, organophosphorus-tellurium heterocycles (RP)$_n$Te$_m$ have been only sporadically investigated.$^3$ The systems were usually obtained as mixtures and characterized by a combination of solution-state $^{31}$P and $^{125}$Te NMR as well as mass spectrometry.$^6,9$

The different synthetic approaches that were developed to generate organophosphorus(III)-tellurium heterocycles include reactions of (a) RP–Si reagents [R = tBu] with tellurium,$^5,7$ (b) RPCI$_2$ [R = tBu, R’$_2$N (R’ = tPr, Cy, Ph)] with Na$_2$Te, Li$_2$Te$_2$ or Te(SiMe$_3$)$_2$,$^{6,9}$ (c) tBuCl–P(Cl)tBu with Na$_2$Te,$^5,6$ or (d) nBu$_2$PTe with the diphenosphine TbtP=PFe (Tbt = 2,4,6-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 Monet$^8,7$, Karaghiosoff$^{8,9}$ and Tokitoh$^{10}$ lead to the following conclusions:

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

(ii) stable heterocycles containing both terminal (endo) Te atoms, i.e. a P=Te(µ-Te) unit, cf. LR and WR, are unlikely

(iii) 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

(iv) the pure 3- and 4-membered rings that were isolated (tBuP)$_n$Te (n = 2, 3) are yellow or red liquids at RT

(v) the reported compounds are air-sensitive, some show light-sensitivity and thermal instability, which complicates the isolation and characterization

(vi) no solid-state structures have been reported.

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. Te$_3$(PR)$_n$ (R = Mes*, Trt; Trt = trityl = –CPh$_3$), (b) the first solid-state structural characterizations of Te$_n$(RP)$_m$ rings including Te$_3$(PR)$_3$ (R = OMe*$), Te(KR)$_3$ (R = Ad) Te(PR)$_3$ (R = Fc), and (c) P$_2$N$_2$-stabilized organophosphorus(III)-tellurium rings.

Figure 1. Structural arrangements of organophosphorus(III)-tellurium heterocycles (RP)$_n$Te$_m$, including this work. The existence of Te$_3$(RP)$_3$ is tentative based on limited NMR data.$^7$

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Supporting information for this article is available on the WWW.
Results and discussion

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

The first synthetic approach involves the reaction of RPCl₂ (R = Fe, Ad, Mes*O, Mes*, Tri) with Na₂Te₂ in THF (Scheme 1). These R groups were chosen since they provide significant steric bulk (Mes*, Tri) and the Fe 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-butylic ligands. The reactions of the adamantyl-substituted compounds are usually slower but crystallization is favored in comparison to tert-butylic 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) FcPCl₂ and (b) AdPCl₂ with Na₂Te₂ in THF.](image)

Treatment of FcPCl₂ with an equimolar amount of Na₂Te₂ in THF at −78 °C produced 1a as the major product with the cyclopentaphosphane (FcP)₂ as a by-product, which was identified by X-ray crystallography. The 2,3,4,5-tetra-tert-butylic-1-telluric-2,3,4,5-tetraphosphane 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 AdPCl₂ with Na₂Te₂ under similar conditions yielded the telluridiphosphirane 2b as the main product and the telluratriphosphetane 2a as a minor product (³¹P NMR); 2a was isolated as red crystals in ca. 5% yield.

![Scheme 2. Reaction of Mes*OPCl₂ with Na₂Te₂ in THF.](image)

Similarly Mes*OPCl₂ was reacted with Na₂Te₂ to yield the telluridiphosphirane 3a, which was isolated in a yield of 37% after recrystallization from hexane. Finally, the reaction of Mes*PCl₂ and TrtPCl₂ with an equimolar amount of Na₂Te₂ gave rise to the novel tritelluratriphosphorinanes 4a (Mes*PTe₂) and 5a (TrtPTe₂), which were characterized by NMR spectroscopy. For the reaction with Mes*PCl₂ the disphosphene (Mes*P=PMes*) 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 TrtPCl₂ reactions a telluratriphosphetane 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.

Figure 2. ³¹P NMR spectrum (202.47 MHz) of 1a: (A) AA’MM’ spectrum calculated by iterative fitting, (B) experimental spectrum.10 The P1/P1’ resonances appear at 84.5 ppm revealing a Jₚ₋₁₋₂₂ coupling of −305.1 Hz, a Jₚ₋₁₋₂₂ coupling of 31.0 Hz and a Jₚ₋₁₋₁₂ coupling of 8.0 Hz. The P2/P2’ resonances are observable at 69.6 ppm with a Jₚ₋₆₋₂₂ coupling of −339.0 Hz.12 The very poor solubility of 1a precluded the observation of ¹²⁵Te satellites as well as characterization by ¹²⁵Te NMR. The adamantyl derivative 2a shows a first order A₂M-type ³¹P NMR spectrum (considering the ¹²⁵Te-containing isotopomer it expands to an A₂M’M’X spin system). The characteristic values (shift and coupling constants) were calculated by iterative fitting as shown in Figure 2.

Scheme 3. Reaction of d) Mes*PCl₂ and e) TrtPCl₂ with Na₂Te₂ in THF.

The ¹²⁵Te NMR spectrum of 1a exhibits a second order AA’MM’ pattern (considering the ¹²⁵Te-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.
A single resonance at 78.5 ppm is observed in the $^{31}\text{P}$ NMR spectrum of 3a (as in 2b a $\text{A}_2\text{X}$ 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 $J_{\text{P}-\text{Te}}$ of 396.9 Hz which is quite high compared to 2b or the reported derivatives by du Mont et al. (229 Hz), Tokiho et al. (260 Hz) or Karaghiosoff et al. (285.2 Hz). The observations are consistent with the simulation of an A$^1$TeN NMR spectrum at 7.7 ppm, which also shows a significantly low field shift when compared to the other reported P$_2$Te$_2$-systems and 2b.

![Figure 3](image1.png)

Figure 3. $^{19}$F NMR spectra (109.3 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 $J_{\text{P}-\text{Te}}$ values are rather large with $-441.7$ Hz (4a) and $-398.7$ Hz (5a) respectively (negative signs are derived from iterative fitting). The $J_{\text{P}-\text{P}}$ values were shown to be $325.0$ Hz (4a) and $257.1$ Hz (5a). $J_{\text{P}-\text{P}}$ could not be observed. The large $J_{\text{P}-\text{P}}$ 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$_2$Te$_2$ 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](image2.png)

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 telluratricophosphatane 5b shows two resonances, a doublet at 131.8 ppm and a triplet at 82.1 ppm. In comparison to 2a a small $J_{\text{P}-\text{P}}$ coupling is visible at 72.2 Hz, in the form of satellites at the doublet. The $J_{\text{P}-\text{P}}$ value of 187.0 Hz is slightly larger than for 2a (169.0 Hz) or the $\text{Bu}$ substituted derivative (172.6 Hz) but smaller than those with CF$_3$ substituents (248.7 Hz).

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

Crystals of 2,3,4,5-tetra-ferrocenyl-1-tellura-2,3,4,5-tetraphospholane 1a were isolated from toluene at $-40$ °C as red prisms. The crystal structure of 1a (Figure 5) reveals that the P$_2$Te 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 P$^{III}$Te single bond in the acyclic compound Te(P(Ph)$_3$)$_3$. The observed P–Te bond lengths of 2.188(8) Å and 2.163(8) Å are slightly shorter than those in the related cyclo-pentaphosphane (FcP)$_4$.

![Figure 5](image3.png)

Figure 5: A: X-ray crystal structure of 1a. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Tel–P1 2.503(6), P1–P2 2.188(8), P2–P2' 2.163(8), P1–Cl1 1.84(3), P2–C11 1.83(3), P1–Tel–P1 1.04.89(19), Tel–P1–P2 1.00.9(3), Tel–P1–Cl1 94.7(7), P1–P2–P2' 111.2(3), P2–P1–C1 99.4(7), P2–P2–C11 103.3(7). B: packing along the a-axis.

Single crystals of 2,3,4-tris-adamantyl-1-tellura-2,3,4-triphosphatane 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)$_4$:[P(Ad–P) 2.2417(15)-2.2423(15) Å].

The four-membered P$_2$Te-Ring is non-planar and the adamantyl ligands adopt an all-trans conformation (Figure 6). The ring shows a torsion angle of 161.66°, cf. 151.7° in (AdP)$_4$.
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 2.474(9), Te1–P2 2.462(9), P1–P2 2.247(3), P1–Te1 1.663(9), P2–Te1 1.667(9), P1–Te1 2.54(9), P1–Te1 2.54(9), P1–Te1 2.54(9), P2–Te2 2.55(3), Te1–P1–O1 107.5(4), P1–P2–O2 105.6(4).

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 P3Te ring system with comparatively short P–Te distances of 2.462(9)-2.474(9) Å and a slightly longer P–P distance 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 2.483(3), Te2–P2 2.508(3), Te3–P3 2.474(3), Te3–P1 2.483(3), Te3–P2 2.491(3), Te4–P4 2.482(3), Te4–P5 2.476(4), Te5–P4 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 83.4(1), P2–Te2–P3 82.52(9), P1–Te3–P3 80.94(9), P4–Te4–P5 81.88(10), P5–Te5–P6 82.51(10), P4–Te6–P6 81.70(10), Te1–P1–Te3 103.62(11), Te1–P2–Te2 104.45(11), Te2–P3–Te3 105.48(11), Te4–P4–Te6 105.67(11), Te4–P5–Te5 105.12(12), Te5–P6–Te6 100.12(12), Te1–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 PSe3Cl3 system in the literature is a PSe3 ring reported by Goldwhite et al.,21 P3Se3 rings are unknown in the literature. The P3Se3 system adopts a chair conformation in contrast to the few examples of P3O3 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(11))°.

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 P3N3-stabilised organophosphorus(III)-tellurium heterocycles

The second synthetic pathway to organophosphorus-tellurium heterocycles utilises the reaction of RPCl3 (R = Ad, tBu with [Li(TMEDA)]2[µ-BuN(Te)(µ-tBu)P(Tc)N(tBu)]23 (Scheme 4), a dianionic reagent that has proved to be effective in the preparation of a cyclic telluridane by metathesis with TeCl2·TMTU.19

Scheme 4. Reaction of [Li(TMEDA)]2[µ-BuN(Te)(µ-tBu)P(Te)N(tBu)] with AdPCl3 and tBuPCl3 in toluene.

The reactions of RPCl3 (R = Ad, tBu) with [Li(TMEDA)]2[µ-BuN(Te)(µ-tBu)P(Tc)N(tBu)] 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 AX2 spin system (with the 125Te-containing isotopomer it expands to an AA’XX type spectrum, where the isochronous P1 and P1’ nuclei become magnetically inequivalent), showing a triplet at 89.5 ppm, 6a, and a doublet at −129.6 ppm (7a).

Interestingly, the one-bond P–Te coupling constants involving P2 and P1 differ remarkably, 1Jp1,Te1 = 420 (6a), 418 Hz (7a) and 1Jp1,Te1 = 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 P3Te compounds in this (vide supra) and previous work6,8,9,24 whereas values > 1.000 Hz are observed for ditellurio derivatives of the P2N2 ring.19,23,25 The 125Te NMR spectra displayed a doublet of
doublets pattern centered at 368.5 (6a), 423.4 ppm (7a) with $1^J_{P-Te}$ values that corroborate those found in the $^{31}P$ NMR spectra.

The molecular structure of 6a (Figure 9) contains a Te–P=II,Te unit bridging a $\text{P}^2\text{N}_2$ ring cf. the derivatives 1,3-Te-(PR)$_3$ (R = tBu, CF$_3$), which have been tentatively identified by NMR spectroscopy. $^7$,$^9$

![Figure 10](image)

**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 1.505(3), 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 105.8(5), Te2–P2–Te1 108.81(6), P1–P2–N1 96.5(5), P1–N3–P1 95.66(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$^2$ 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(PR$_3$)$_2$. 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$_2$-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$_n$PR$_n$, where n > m.

Although Na$_2$Te$_2$ 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–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 Satorf 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 a 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 $^1$H, $^{13}$C($^1$H, $^{31}$P,$^3$H) and $^{125}$Te($^1$H) NMR spectra were recorded using a JEOL DELTA EX 270, a Bruker Avance II 400 or a Bruker Avance III 500 spectrometer. $^{11}$H and $^{125}$Te($^1$H) NMR were referenced to TMS as internal standard, 85% H$_3$PO$_4$ was used as an external standard for $^{13}$C($^1$H) NMR and P$_2$H$_4$ for Te($^1$H/$^3$H) NMR spectra, all NMR data was collected at 25 °C. Mass spectrometry was performed on a MICROMASS LCT (ES) and MICROMASS GCT (EI, Cl) 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 Sauter SMP 30 melting point apparatus.

1a (FeCl$_3$)Te$_2$ in 100 ml Schlenk flask Na$_2$Te$_2$ (525 mg, 1.7 mmol) was suspended in dry THF (10 ml). The suspension was cooled down to -78°C. A solution of FeCl$_3$ (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 (FeCl$_3$) and stored at -20°C overnight to yield 2,3,4,5-tetra-ferrocenyl-1,2,4,5-tetraselenophane as red crystals (yield 9%). $^{31}$P NMR (D$_2$THF): $\delta$ = 84.5 ppm, $|{J(P,Te)}| = 305.1 Hz, $|{J(P,Te)}$| = 310.7 Hz, $|{J(P,Te)}| = 12.0$ Hz, 69.6 ppm, $|{J(P,Te)}| = 310.5$ Hz, $|{J(P,Te)}| = 330.9$ Hz, $|{J(P,Te)}| = 310.7$ Hz ppm. $^{125}$Te NMR (D$_2$THF): $\delta$ = no sharp signals due to low solubility. $M_p$ = 200°C. MS (CI, m/z): 992.9 [M+H$^+$] (calculated: 992.8 [M+H$^+$]). HR-MS [(APCI,APSA)]: 994,908,903 [M+H$^+$]; EA caled (%) for Ca$_3$H$_6$P$_2$Te$_2$: C 48.45, H 8.66, found: C 48.35, H 3.73.

2a (AdPCl)$_2$Te$_2$ and 2b (AdP)$_2$Te: Procedure as for 1a using AdPCl$_2$ (500 mg, 2.1 mmol) and Na$_2$Te$_2$ (451 mg, 1.5 mmol). After 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 in 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 %. $^1$H NMR (D$_2$THF): $\delta$ = 7.31 (s, 2H), 1.50 (s, 18H), 1.33 (s, 9H) ppm. $^{31}$P NMR (D$_2$THF): $\delta$ = 87.8 ppm, $|{J(31P,Te)}| = 396.9$ Hz, $|{J(31P,Te)}| = 332.1$ Hz ppm. $^{125}$Te NMR (D$_2$THF): $\delta$ = 7.7 ppm. $|{J(125Te)}| = 394.6$ Hz ppm. $M_p$ = 126 °C (dec). MS (EI, m/z): 628.2 [M$^-$] (calculated: 628.2 [M$^-$]).

3a (MesOPCl)$_2$Te: Procedure as for 1a using MesOPCl$_2$ (500 mg, 1.4 mmol) and Na$_2$Te$_2$ (415 mg, 1.5 mmol). After 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 in 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 %. $^1$H NMR (D$_2$THF): $\delta$ = 7.31 (s, 2H), 1.50 (s, 18H), 1.33 (s, 9H) ppm. $^{31}$P NMR (D$_2$THF): $\delta$ = 87.8 ppm, $|{J(31P,Te)}| = 396.9$ Hz, $|{J(31P,Te)}| = 332.1$ Hz ppm. $^{125}$Te NMR (D$_2$THF): $\delta$ = 7.7 ppm. $|{J(125Te)}| = 394.6$ Hz ppm. $M_p$ = 126 °C (dec). MS (EI, m/z): 628.2 [M$^-$] (calculated: 628.2 [M$^-$]).
removed under vacuum. The obtained solid was dissolved in hexane and maintained at −40°C overnight. The red deep 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%). 1H NMR (CD2Cl2): δ = 1.98 (m, 9H, Ad) 1.82 (s, 9H, Ar), 1.73 (s, 9H, Bu), 1.47 (s, 18H, Bu), 2.02 (6, 18H, Ad). 13C NMR (CD2Cl2); δ = 189.5 (1, 13C, Pd), 17.0 (6, 18C, Ad), 11.0 (6, 18C, Bu), 42.7 (1, 13C, Pd). 19F NMR (CD2Cl2); δ = −198.6 (1, 13C, Pd), 197.0 (1, 13C, Pd). The compound was found to be a mixture of cis and trans isomers (δ = 6.07 and 6.12 ppm respectively) as confirmed by 2D NMR. HRMS (quadrupole); m/z calcd 769.1 [M+H]+; found 769.1 [M+H]+

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Entry for the Table of Contents

Layout 2:

Isolatable
organophosphorus(III)-tellurium heterocycles

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Page – Page

Isolatable
organophosphorus(III)-tellurium heterocycles

Organophosphorus(III)-tellurium heterocycles can be stabilized and structurally characterized by (a) the appropriate choice of substituents in $\text{Te}_{m}(\text{P}^{\text{III}}\text{R})_{n}$ ($m = 1$: $n = 2$, $R = \text{OMes}^*$; $n = 3$, $R = \text{Ad}$; $n = 4$, $R = \text{Fc}$; $m = n = 3$: $R = \text{Trt, Mes}^*$) or (b) the installation of a $\text{P}^{\text{V}}_{2}\text{N}_{2}$ anchor in $\text{RP}^{\text{III}}\text{TeP}^{\text{V}}(\text{tBuN})(\mu-\text{NtBu})_{2}$ ($R = \text{Ad, tBu}$).