

Electronic Supplementary Information

Successful oxidation of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2, 4, 6$) by tellurium leading to $\text{Ph}_2\text{P}(\text{Te})(\text{CH}_2)_n\text{P}(\text{Te})\text{Ph}_2$

Lukáš Jeremias,^a Michal Babiak,^a Václav Kubát,^a Maria José Calhorda,^b Zdeněk Trávníček,^c and Josef Novosad^{*a,b}

^a Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic. Fax: +420549492443; Tel: +420549496202; E-mail: novosad@chemi.muni.cz

^b Departamento de Química e Bioquímica, CQB, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Ed. C8, PT-1749-016 Lisboa, Portugal.

^c Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, CZ-77146 Olomouc, Czech Republic.

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Details of the syntheses

Weights of the starting components for **1**: 100 mg $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (0.251 mmol), 64 mg Te (0.50 mmol); **2**: 100 mg $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (0.234 mmol), 60 mg Te (0.47 mmol); **3**: 100 mg $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$ (0.220 mmol), 56 mg Te (0.44 mmol).

Yields – **1**: 2-3 % (3-5 mg, 0.005-0.008 mmol); **2**: 3-5 % (4-6 mg, 0.007-0.01 mmol); **3**: 4-6 % (6-9 mg, 0.008-0.01 mmol).

Chemicals

Chemicals used for synthesis were purchased from Sigma-Aldrich (Te, 99,8%, –200 Mesh; 1,2-bis(diphenylphosphino)ethane, 97%; 1,4-bis(diphenylphosphino)butane, 98%; 1,6-bis(diphenylphosphino)hexane, 97%), and were used without further purification. Toluene and petroleum ether (Penta, p.a.) were stored over sodium wire.

Product characterization

Elemental analyses were carried out on a Flash 2000 CHNS Elemental Analyzer (Thermo Scientific).

$^{31}\text{P}\{^1\text{H}\}$ and ^{125}Te NMR were recorded on a Bruker Avance III 500 MHz spectrometer operating at frequency of 202.45 MHz (^{31}P), with chemical shifts reported relative to 85% H_3PO_4 (^{31}P). ^{125}Te NMR spectra were measured at 157.78 MHz and were referenced against secondary standard (*p*- MeOC_6H_4) $_2\text{TeCl}_2$ (chemical shift 933.1 ppm relative to 0 ppm of suggested primary standard (Me_2Te)¹⁶). Chemical shifts are reported in parts per million (ppm).

Discussion of NMR spectra

Compound **1** seems to decompose in solution very easily before NMR spectra can be collected. Still, in ^{125}Te NMR spectrum one singlet at -653.0 ppm was observed and in ^{31}P NMR spectrum one doublet ($^3J(^{31}\text{P}, ^{31}\text{P}) = 52.2$ Hz) with chemical shift 32.5 ppm was detected apart from the singlet of unoxidized phosphorus(III) atom at -11.4 ppm.

Neither tellurium satellites in phosphorus spectra, nor splitting of signals to doublets in tellurium spectra was observed. Due to the presence of unoxidized ligands in the sample we presume this can be explained by rapid exchange of tellurium atoms between PCP ligands, as described in literature.^{8,15}

The presence of two nonequivalent phosphorus atoms shown by the doublet in the ^{31}P NMR spectrum indicates that monotelluro species $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Te})\text{Ph}_2$ are formed in solution of **1**. After the NMR experiment, solvent from the NMR sample of **1** was evaporated. The resulting solid was dissolved in 3 ml of toluene and 10 ml of petroleum ether was added to the solution. The mixture was thoroughly mixed and cooled to -27 °C. After a few days, yellow crystals were obtained. These crystals were identified by single-crystal X-ray analysis as ditelluro species $\text{Ph}_2\text{P}(\text{Te})(\text{CH}_2)_2\text{P}(\text{Te})\text{Ph}_2$ (**1**).

Compound **2** showed two singlets in ^{31}P NMR spectrum. The signal at 33.0 ppm belongs to phosphorus(V) atom of the $\text{P}=\text{Te}$ moiety. The second signal with chemical shift -12.5 ppm belongs to the unoxidized phosphorus(III) atom in $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{P}(\text{Te})\text{Ph}_2$ and in $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, which was present in the sample due to spontaneous decomposition of part of the product.

Analogous ^{31}P NMR spectrum was collected for compound **3**: two singlets with chemical shifts 33.0 ppm (P^{V}) and -12.1 ppm (as in **2**, decomposition of part of the product took place) are observed.

In the ^{125}Te NMR spectrum one singlet was observed in both cases, at -636.5 ppm for compound **2** and -641.4 ppm for **3**.

The rapid exchange of Te atoms between PCP ligands has to be considered again.

Typical NMR spectra are shown in Fig. S1 ($^{31}\text{P}\{^1\text{H}\}$ NMR, compound **3**) and Fig. S2 (^{125}Te NMR, compound **3**).

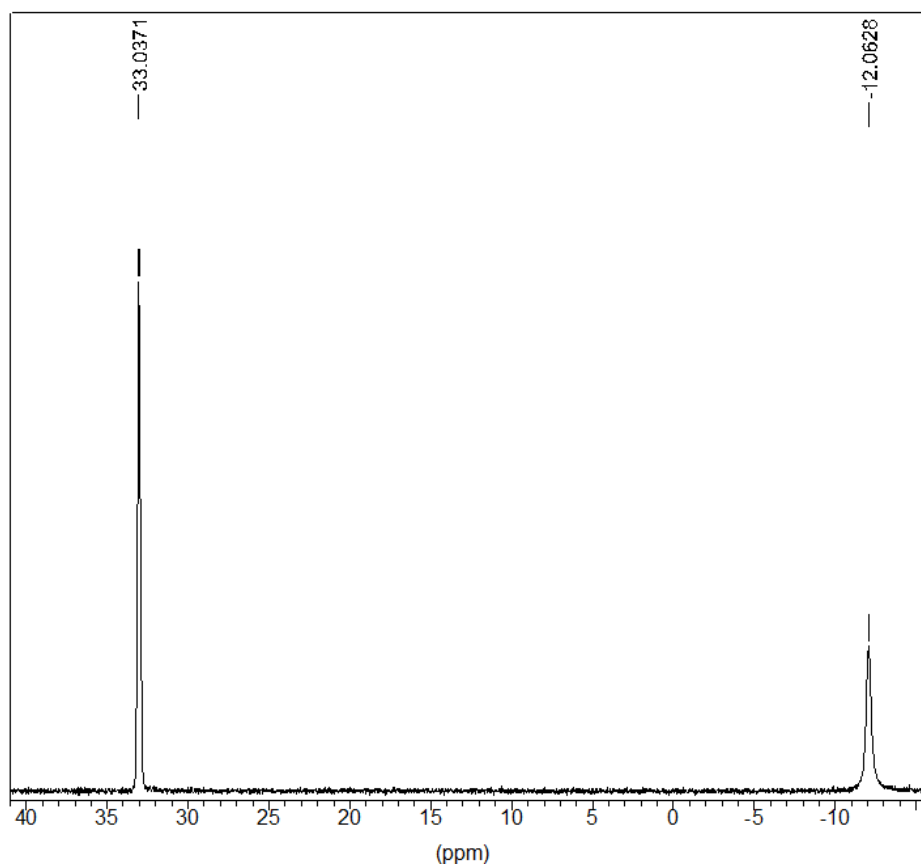


Fig. S1: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 3.

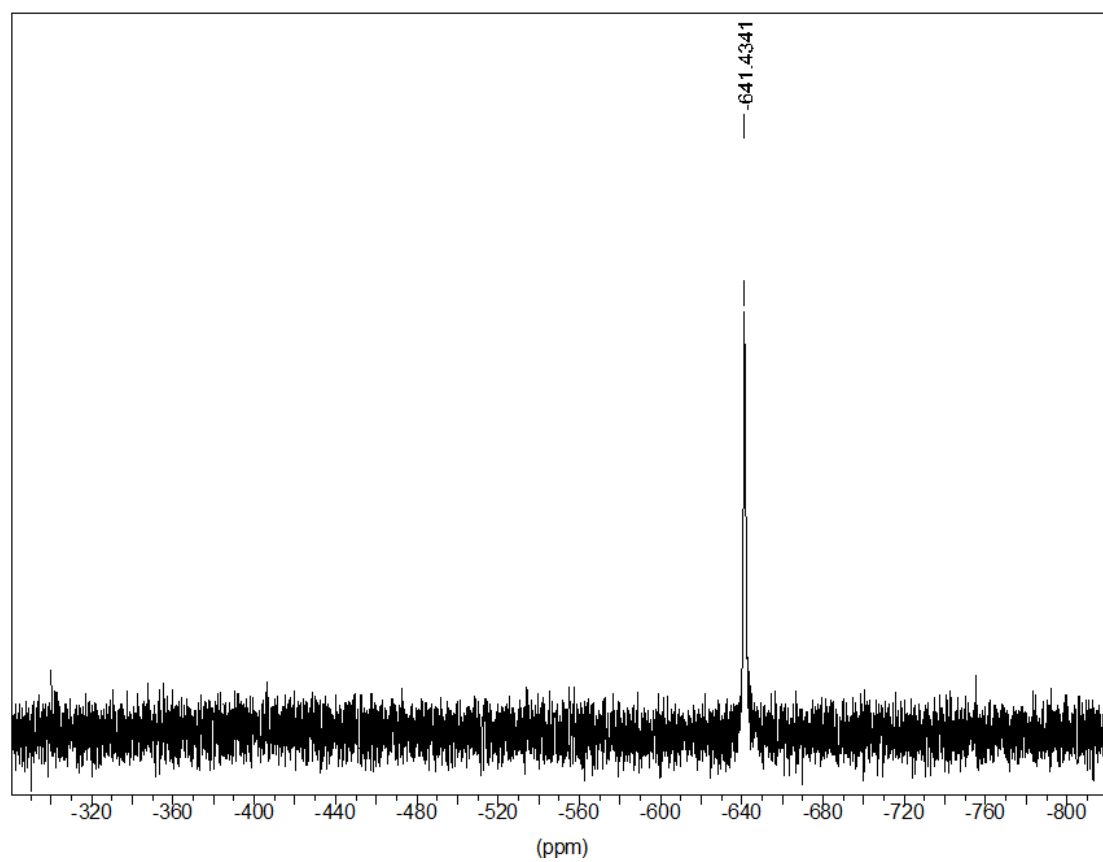


Fig. S2: ^{125}Te NMR spectrum of compound 3.

Product characterizations by single crystal X-ray diffraction

Diffraction data were collected on a KUMA KM-4 κ -axis CCD diffractometer with Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$), at 120(2) K. Proper collection strategy was calculated by internal strategy module of CrysAlis CCD.¹⁷ Data were then reduced using CrysAlis RED.¹⁸

Locations of heavy atoms were determined using Patterson algorithm of SHELXS program¹⁹, then the other non-hydrogen atoms were located in difference Fourier maps and models were refined using SHELXL.¹⁹

All hydrogen atoms were placed at calculated positions and were refined as riding (using SHELXL default effective C–H distances for T = 120 K), with their U_{iso} set to $1.2U_{\text{eq}}$ of the corresponding carbon atom.

Solution and refinement of **2** was not straightforward. At the early stages of the refinement, motifs of $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ could be observed, bridged via intermolecular P1–Te1–P3–P2 moieties, with atypical atomic displacement parameters and atypical P2–P3 and P3–Te1 bond lengths, which did not make chemical sense. Considering the monosubstituted product, the P3 atom was refined as tellurium Te1B, with the site occupancy factor (sof) of both Te1A and Te1B also refined. Refinement converged to $\text{sof}(\text{Te1A}) = 0.77302$ and $\text{sof}(\text{Te1B}) = 0.20693$, the sum of these values being equal to 0.97995. Then, the sum of these two site occupancy factors was constrained to be equal to one and the bond lengths P1–Te1A and P2–Te1B were restrained to be equal with an effective standard deviation. The aliphatic butylene moiety is also disordered. This was treated by constraining the sum of site occupancy factors of corresponding atoms to one. Atoms C1 and C4 are treated as two sets of atoms (C1A and C1B, C4A and C4B) with identical positions and thermal ellipsoids, because of hydrogen treatment. Free variable describing the sof of atoms of butane-1,4-diyl moiety converged to approximately same value as free variable describing tellurium disorder. These two free variables were then merged into single free variable. Resulting site occupancy factors can be found in supplied crystallographic information files.

Considering disorder and weak intermolecular interactions between phosphorus and tellurium, the structure of **2** could be interpreted as an ordered linear polymer of $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{P}(\text{Te})\text{Ph}_2$, where approximately 21% of chains would be inverted (which concerns the locations of Te, C2 and C3 atoms and hydrogen atoms of butane-1,4-diyl moiety). This non-centrosymmetric structure is further complicated by the fact, that crystal is an inversion twin (with approximately 54.5 % of the major twin component). The notable difference in bond lengths ($2.3491(9) \text{ \AA}$ for P1–Te1A, $2.2416(14) \text{ \AA}$ for P2–Te1B), which could not be reasonably treated by soft restraints, can be explained by effects of Fourier truncation near the average position of disordered heaviest atom.

Specific crystal data follow. Bond lengths, angles and other details can be found in supplied crystallographic information files.

Crystal data and structure refinement for $\text{Ph}_2\text{P}(\text{Te})(\text{CH}_2)_2\text{P}(\text{Te})\text{Ph}_2$, 1

Crystal data

$\text{C}_{26}\text{H}_{24}\text{P}_2\text{Te}_2$	$F(000) = 1256$
$M_r = 653.59$	$D_x = 1.769 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Melting point: 364 K
Hall symbol: $-C 2yc$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 17.383 (4) \text{ \AA}$	Cell parameters from 3116 reflections
$b = 9.831 (3) \text{ \AA}$	$\theta = 2.8\text{--}27.7^\circ$
$c = 14.5721 (9) \text{ \AA}$	$\mu = 2.52 \text{ mm}^{-1}$
$\beta = 99.732 (12)^\circ$	$T = 120 \text{ K}$
$V = 2454.3 (9) \text{ \AA}^3$	Block, yellow
$Z = 4$	$0.20 \times 0.20 \times 0.13 \text{ mm}$

Data collection

Xcalibur, Sapphire2, large Be window diffractometer	2416 independent reflections
Radiation source: sealed X-ray tube, Enhance (Mo) X-ray Source	1997 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.013$
Detector resolution: $8.4353 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.8^\circ$
ω scan	$h = -21 \rightarrow 15$
Absorption correction: multi-scan <i>CrysAlis RED</i> (Oxford Diffraction Ltd, 2009)	$k = -12 \rightarrow 9$
$T_{\text{min}} = 0.633$, $T_{\text{max}} = 0.735$	$l = -17 \rightarrow 15$
4737 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: heavy-atom method
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.017$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.038$	H-atom parameters constrained
$S = 0.96$	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2]$
2416 reflections	where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	$(\Delta/\sigma)_{\text{max}} = 0.002$
0 restraints	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Crystal data and structure refinement for $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{P}(\text{Te})\text{Ph}_2$, 2

Crystal data

$\text{C}_{28}\text{H}_{28}\text{P}_2\text{Te}$	$F(000) = 556$
$M_r = 554.04$	$D_x = 1.496 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Melting point: 373 K
Hall symbol: P 2yb	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 9.0157 (4) \text{ \AA}$	Cell parameters from 6388 reflections
$b = 14.2910 (7) \text{ \AA}$	$\theta = 2.8\text{--}27.8^\circ$
$c = 9.7134 (4) \text{ \AA}$	$\mu = 1.35 \text{ mm}^{-1}$
$\beta = 100.562 (4)^\circ$	$T = 120 \text{ K}$
$V = 1230.30 (10) \text{ \AA}^3$	Block, yellow
$Z = 2$	$0.40 \times 0.40 \times 0.35 \text{ mm}$

Data collection

Xcalibur, Sapphire2, large Be window diffractometer	3937 independent reflections
Radiation source: sealed X-ray tube, Enhance (Mo) X-ray Source	3788 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.031$
Detector resolution: $8.4353 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.9^\circ$
ω scan	$h = -10 \rightarrow 10$
Absorption correction: multi-scan <i>CrysAlis RED</i> (Oxford Diffraction Ltd, 2009)	$k = -16 \rightarrow 16$
$T_{\text{min}} = 0.614$, $T_{\text{max}} = 0.649$	$l = -11 \rightarrow 11$
8099 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: heavy-atom method
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.057$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2]$
3937 reflections	where $P = (F_o^2 + 2F_c^2)/3$
309 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
32 restraints	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Crystal data and structure refinement for $\text{Ph}_2\text{P}(\text{Te})(\text{CH}_2)_6\text{P}(\text{Te})\text{Ph}_2$, 3

Crystal data

$\text{C}_{30}\text{H}_{32}\text{P}_2\text{Te}_2$	$Z = 2$
$M_r = 709.70$	$F(000) = 692$
Triclinic, $P1$	$D_x = 1.561 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Melting point: 390 K
$a = 9.513 (2) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 12.852 (3) \text{ \AA}$	Cell parameters from 6769 reflections
$c = 13.247 (3) \text{ \AA}$	$\theta = 3.0\text{--}27.7^\circ$
$\alpha = 100.80 (2)^\circ$	$\mu = 2.05 \text{ mm}^{-1}$
$\beta = 100.66 (2)^\circ$	$T = 120 \text{ K}$
$\gamma = 102.393 (18)^\circ$	Block, yellow
$V = 1510.4 (6) \text{ \AA}^3$	$0.43 \times 0.20 \times 0.13 \text{ mm}$

Data collection

Xcalibur, Sapphire2, large Be window diffractometer	5940 independent reflections
Radiation source: sealed X-ray tube, Enhance (Mo) X-ray Source	4687 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.018$
Detector resolution: $8.4353 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
ω scan	$h = -11 \rightarrow 11$
Absorption correction: multi-scan <i>CrysAlis RED</i> (Oxford Diffraction Ltd, 2009)	$k = -13 \rightarrow 15$
$T_{\text{min}} = 0.472$, $T_{\text{max}} = 0.776$	$l = -16 \rightarrow 15$
11693 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: heavy-atom method
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.094$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 1.5127P]$ where $P = (F_o^2 + 2F_c^2)/3$
5940 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
307 parameters	$\Delta\rho_{\text{max}} = 1.87 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$

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