

Fifth draft April 10, 2012-TC

**A cyclic tritelluride and a planar dianionic ditelluride supported by
P₂N₂ rings[†]**

**Andreas Nordheider,^{a,b} Tristram Chivers,^{a*} Ramalingam Thirumoorthi,^a Alexandra
M. Z. Slawin^b and J. Derek Woollins^b**

^a *Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4.*

E-mail: chivers@ucalgary.ca; Fax: +1 403-289-9488; Tel: +1 403-220-5741

^b *Department of Chemistry, University of St Andrews, St Andrews UK, KY16 9ST*

[†] Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC references numbers xxxxxx ([Na(tmeda)]₂**3**), yyyyyy (**4**) and zzzzz ([Li(tmeda)]₂**5**).

Oxidation of alkali metal derivatives of the dianion $[\text{TeP}_2\text{N}_2\text{Te}]^{2-}$ [$\text{P}_2\text{N}_2 = (\text{tBuN})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{N}^t\text{Bu})$] with I_2 produces the cyclic tritelluride $[\text{P}_2\text{N}_2(\mu\text{-Te-Te-Te})]$; the intermediate ditelluride $[\text{TeP}_2\text{N}_2\text{TeTeP}_2\text{N}_2\text{Te}]^{2-}$ with a planar $\text{P}\text{Te}\text{Te}\text{P}$ conformation has also been characterised.

There is a dearth of information on phosphorus-tellurium heterocycles compared with their relatively well-studied sulfur or selenium analogues.¹⁻³ Although several organophosphorus(III)-tellurium heterocycles of the type cyclo- $(\text{RP})_x\text{Te}_y$ ($x > y$) have been prepared, characterization has been limited to ^{31}P and ^{125}Te NMR spectra or mass spectrometric data.⁴⁻⁹ We and others have shown that terminal P-Te bonds are stabilized by an anionic charge^{10,11} and that property is manifested in the recent report of the synthesis and NMR characterization of the first binary P-Te anion $[\text{P}_4\text{Te}_2]^{2-}$.¹²

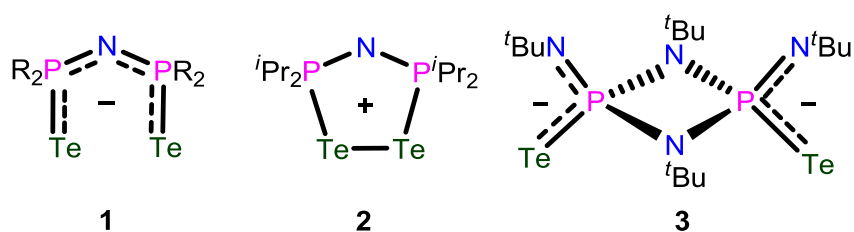
In our studies of the oxidation of the acyclic monoanions $[\text{TePR}_2\text{NPR}_2\text{Te}]^-$ (**1**, $\text{R} = \text{tPr}, \text{tBu}$) we found that one-electron oxidation with I_2 results in formation of ditellurides, which may adopt either acyclic or spirocyclic structures;^[13,14] two-electron oxidation generates the cyclic cation $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]^+$ (**2**), which incorporates a five-membered $\text{NP}(\text{V})_2\text{Te}_2$ ring.^[15] The facility with which these transformations occur led to consider whether macrocycles in which ditellurido linkages -Te-Te- are bridged by $\text{P}(\text{V})_2\text{N}_2$ scaffolds might be generated by mild oxidation of the dianion $[\text{TeP}_2\text{N}_2\text{Te}]^{2-}$ [$\text{P}_2\text{N}_2 = (\text{tBuN})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{N}^t\text{Bu})$] (**3**).¹⁰ In a recent communication we showed that this strategy leads to the preferential formation of the cyclic trimers $(\text{-P}_2\text{N}_2\text{-E-E-})_3$ ($\text{E} = \text{Se}, \text{S}$) with a planar P_6E_6 framework in the case of the selenium and sulfur analogues.¹⁶ By contrast, we report here that the oxidation of **3** with I_2

Comment [D1]: V? better as P^v to reduce confusion?

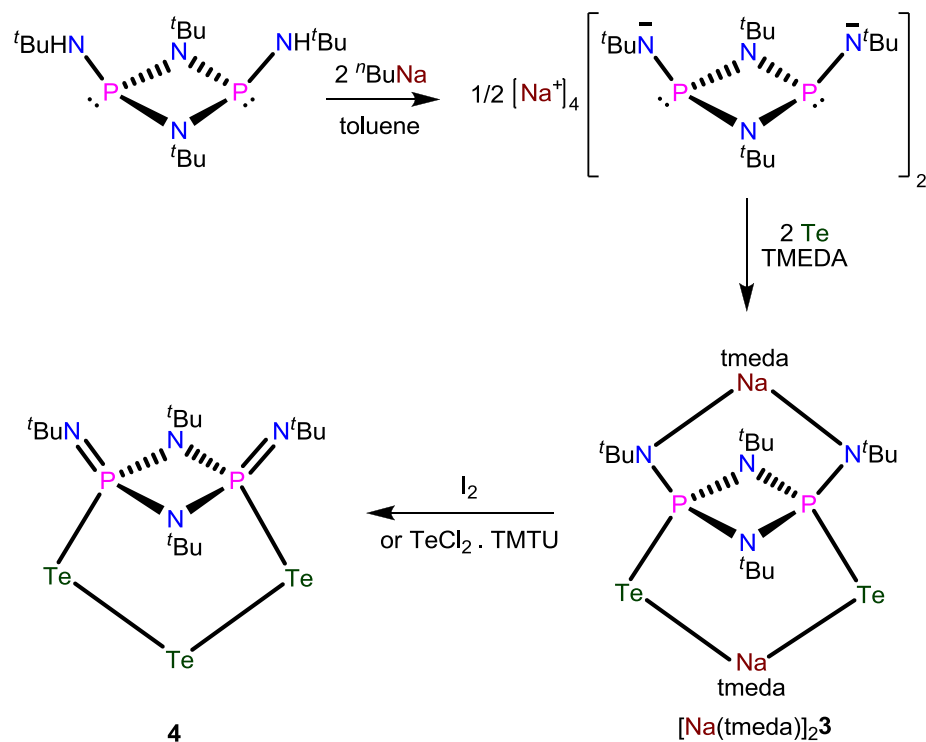
Formatted: Highlight

Formatted: Highlight

produces the cyclic tritelluride $[\text{P}_2\text{N}_2(\mu\text{-Te-Te-Te})]$ (**4**), the first neutral phosphorus-tellurium heterocycle to be characterised in the solid state by X-ray crystallography. The dianionic ditelluride $[\text{TeP}_2\text{N}_2\text{TeTeP}_2\text{N}_2\text{Te}]^{2-}$ (**5**) with a planar $\text{P}\text{Te}\text{Te}\text{P}$ conformation has also been identified as a key intermediate in this oxidative transformation.



The sodium salt $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ was obtained as an extremely air- and moisture-sensitive yellow solid in 67 % yield via the metallation-telluration sequence illustrated in Scheme 1.^{17 †} Crystals of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ suitable for an X-ray analysis were obtained from *n*-hexane at $-30\text{ }^\circ\text{C}$ and the molecular structure is illustrated in Fig. 1.[§] In contrast to the lithium analogue $[\text{Li}(\text{thf})]_2[\mathbf{3}]$ in which the dianionic ligand is coordinated to the Li^+ cations asymmetrically (Te, Te' and N, Te chelation),^{10a} the sodium salt $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ adopts a symmetrical structure (Te, Te' and N, N' coordination), presumably as a result of the larger size of Na^+ .¹⁸ The mean P–Te distance of $2.420(2)\text{ \AA}$ in $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ is shorter by ca. 0.03 \AA than that involving the two-coordinate Te in $[\text{Li}(\text{thf})]_2[\mathbf{3}]$ ^{10a}. Consistently, the $^1J(\text{P}, \text{Te})$ coupling constant of 1583 Hz for $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ is substantially larger than the values of 1309 and 1467 Hz found for the lithium analogue.^{10a} A doublet is observed in the ^{125}Te NMR spectrum of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ at -148.7 ppm , *cf.* -289 and -87 ppm for the inequivalent Te environments in $[\text{Li}(\text{thf})]_2[\mathbf{3}]$.¹⁰



Scheme 1 Synthesis of the cyclic tritelluride **4**

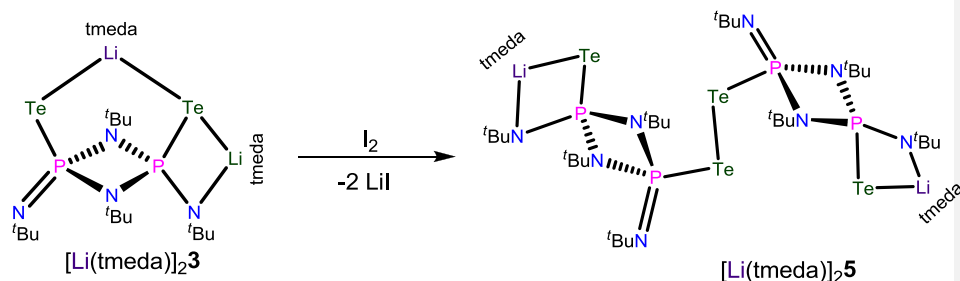
The treatment of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ with an equimolar quantity of I_2 in toluene led to the isolation of a dark red-black solid, which was recrystallised from pentane to give black crystals that were subsequently identified as the tritelluride $[\text{P}_2\text{N}_2(\mu\text{-Te-Te-Te})]$ (**4**) by single-crystal X-ray analysis (*vide infra*). Higher yields (41 %) of **4** are obtained via metathesis of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$ with $\text{TeCl}_2 \cdot \text{tmtu}$ ($\text{tmtu} =$ tetramethylthiourea) in toluene (Scheme 1).[‡]

As shown in Fig. 2 the molecular structure of **4**[§] is comprised of a tritelluride ligand bridging the P₂N₂ ring.[§] To our knowledge, the only other structurally characterised cyclic tritelluride is the binuclear Sn(IV) complex [ArSn(μ-Te)₂(μ-TeTeTe)SnAr] (Ar = 2,6-bis(2,4,6-triisopropylphenyl)phenyl).¹⁹ The structurally characterised acyclic tritellurides incorporate either bulky substituents RTeTeTeR (R = C(SiMe₃)₃)²⁰ or intramolecular N...Te coordination (2-pyridyl-C₆H₅,²¹ 8-Me₂NC₁₀H₇)²²; the structure of the thermally unstable dication [tBu₃PTeTeTeP'tBu₃]²⁺ has also been reported.²³ The mean Te–Te bond length of 2.716 (1) Å and Te–Te–Te bond angle of 104.50(1)° in **4** are comparable to the corresponding values of 2.705 (2) Å and 104.02 (5)° found for [ArSn(μ-Te)₂(μ-TeTeTe)SnAr].¹⁹ The P–Te bond length of 2.536 (1) Å in **4** is notably longer (by ca. 0.12 Å) than the mean value for [Na(tmeda)]₂**3** indicating a weak P–Te bond in **4**. Consistently, the ¹J(P,Te) coupling of 1030 Hz observed in both the ³¹P and ¹²⁵Te NMR spectra of **4** in *d*₈-toluene is among the lowest reported for P–Te compounds.²⁴ The ¹²⁵Te NMR spectrum of **4** is comprised of a well-separated pseudo-doublet of doublets at –442.8 ppm (¹J(P,Te) = 1031 Hz, ³J(P,Te) = 41 Hz), and a pseudo-triplet centred at +361.9 (t, ²J(P,Te) = 35 Hz); these resonances are assigned to the equivalent pair of tellurium atoms Te1, Te2 and the unique tellurium centre Te3, respectively (Fig. 2).

In an attempt to understand the pathway for the formation of the tritelluride **4** we investigated the oxidation of the dianion **3** (as its dilithium derivative)^{10a} with a one-half molar equivalent of I₂. Interestingly, partial oxidation led to the isolation of black crystals, which were identified by X-ray crystallography as [Li(tmeda)]₂**5** (Scheme 2).

[§] As depicted in Fig. 3, the dianion [TeP₂N₂TeTeP₂N₂Te]²⁻ (**5**) is comprised of a

central ditellurido unit that links two P₂N₂ rings, each of which has exocyclic Te and N^tBu substituents that are *N,Te*-chelated to the tmeda-solvated Li⁺ counterions. The Te–Te bond length of 2.755 (3) Å in **5** can be compared with values of 2.70–2.71 Å for typical aryl ditellurides,²⁵ 2.75–2.76 Å for ditellurides supported by an intramolecular Te···N interaction,²⁶ and 2.77 Å for the sterically protected derivative (TpsiTe)₂ (Tpsi = tris(phenyldimethylsilyl)methyl).²⁷ Unusually, the ditelluride **5** is perfectly planar (<P–Te–Te–P = 180.0 °). The only other examples of antiperiplanar ditellurides are deep blue bis(chloro-2-pyridyl) ditelluride,²⁸ red diacyl ditelluride (2-MeOC₆H₄COTe)₂,²⁹ and green (TpsiTe)₂ for which the antiperiplanar conformation is imposed by the bulky substituents.²⁷ In the case of **5**, the planar conformation seems more likely to be attributable to the weak intramolecular Te···Te interactions (3.889 Å), cf. sum of van der Waals radii for Te = 4.12 Å),³⁰ since the closely related neutral ditelluride (H)P₂N₂TeTeP₂N₂(H) (**6**), which has a similar steric environment for the TeTe linkage, exhibits a dihedral angle of ?? °.³¹



Scheme 2. Formation of the dianionic ditelluride **5**

The identification of the dianionic ditelluride **5** as the initial oxidation product of the dianion **3** is reminiscent of the formation of Te-Te bonds (neutral ditellurides) upon one-electron oxidation of the acyclic monoanions **3** (R = *i*Pr, *t*Bu) with I₂.^{13, 14} Importantly, subsequent generation of oligomers of the type (–P₂N₂–Te–Te–)_n via oxidation of **5** can be envisaged, but further investigations are necessary to determine whether such oligomers are thermodynamically unstable with respect to the formation of the cyclic tritelluride **4**.

In summary, the cyclic tritelluride **4** is obtained upon oxidation of the ditellurido P₂N₂-bridged dianion **3** with I₂ and, more efficiently, by metathesis of **3** with TeCl₂·tmtu. The identification of **5** as an initial product of this transformation provides important insights into the oxidation pathway. Both the tritelluride **4** and the dianion ditelluride **5** offer considerable scope for new phosphorus-tellurium chemistry either through detelluration and oxidative additions in the case of **4** or metathetical reactions for **5**.

Notes and references

ⁿBuNa,³² *cis*-(*t*BuNH)P(μ-N^{*t*}Bu)₂P(NH^{*t*}Bu)³³ and TeCl₂·tmtu³⁴ were prepared by the literature procedures.

‡ [Na(tmeda)]₂**3**: Solid ⁿBuNa (0.58 g, 7.2 mmol) was added slowly via a solids dropping funnel to a solution of *cis*-(*t*BuNH)P(μ-N^{*t*}Bu)₂P(NH^{*t*}Bu) (1.00 g, 2.87 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was stirred for 1 h at 23 °C and then for 30 min at 40 °C. Toluene was removed under vacuum and the solid

residue was dissolved in *n*-hexane (20 mL) and filtered to remove unreacted ⁿBuNa. Hexane was removed under vacuum to give [Na₂{^tBuNP(μ-N^tBu)₂PN^tBu}]₂ as a colorless solid (89 % yield).¹⁷ ¹H NMR (*d*₈-toluene, 25 °C): δ = 1.36 (s, 18H, ^tBu), 1.27 (s, 18 H, ^tBu); ³¹P NMR (*d*₈-toluene, 25 °C): δ = 136.5 (s). To a suspension of [Na₄][^tBuNP(μ-N^tBu)₂P(N^tBu)] (0.500 g, 0.64) in toluene (20 mL) was added tellurium powder (0.327 g, 2.56 mmol) and TMEDA (0.305 g, 2.62 mmol). The reaction mixture was stirred for 3 h at 80 °C and then allowed to reach to room temperature. The dark red mixture was filtered and the solvent was removed under vacuum and washed with hexane to give [Na(tmEDA)]₂**3** as a pale yellow solid in 67 % yield.

NMR data for [Na(tmEDA)]₂**3**: ¹H NMR (*d*₈-toluene, 25 °C): δ = 2.04 (s, 24H, NMe₂), 2.01 (s, 18H, ^tBu), 1.85 (s, 8H, CH₂), 1.69 (s, 18H, ^tBu). ³¹P NMR (*d*₈-toluene, 25 °C): δ = -74.9 (s, ¹J(P,Te) = 1590 Hz, ²J(P,P) = 29.6 Hz); ¹²⁵Te NMR (*d*₈-toluene, 25 °C): δ = -148.7(d, ¹J(P,Te) = 1583 Hz).

4: Method A: A solution of iodine (0.145 g, 0.57 mmol) in toluene (15 mL) at -78 °C was added dropwise (15 min) by cannula to a suspension of [Na(tmEDA)]₂**3** (0.500 g, 0.57 mmol) in toluene (20 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C and then at room temperature for 1 h. After filtration toluene was removed under vacuum and the residue was dissolved in *n*-hexane, filtered again and solvent was removed to give a dark red-black solid. Recrystallisation from pentane afforded black crystals of **4** (0.058 g, 14 % yield).

Method B: A solution of TeCl₂·tmtu (0.189 g, 0.57 mmol) in toluene (15 mL) at -78 °C was added dropwise (15 min) by cannula to a suspension of [Na(tmEDA)]₂**3**

(0.500g, 0.57 mmol) in toluene (20 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 3 h at $-78\text{ }^{\circ}\text{C}$ and then for 2 h at room temperature. The precipitate (NaCl) was removed by filtration and solvent was removed from the filtrate under vacuum. (0.195 g, 41 % yield). **Mp. 115-120 $^{\circ}\text{C}$ (dec.) ??**

NMR data for **4**: ^1H NMR (d_8 -toluene, $25\text{ }^{\circ}\text{C}$): 1.65 (s, 18 H, ^tBu), 1.39 (s, 18 H, ^tBu , $^3J(\text{P},\text{H}) = 1.0\text{ Hz}$); ^{31}P NMR (d_8 -toluene, $25\text{ }^{\circ}\text{C}$): $\delta = -134.5$ (s, $^1J(\text{P},\text{Te}) = 1029\text{ Hz}$, $^2J(\text{P},\text{P}) = 31\text{ Hz}$); ^{125}Te NMR (d_8 -toluene, $25\text{ }^{\circ}\text{C}$): $\delta = -442.8$ (dd, $^1J(\text{P},\text{Te}) = 1031\text{ Hz}$, $^3J(\text{P},\text{Te}) = 41\text{ Hz}$), 361.9 (t, $^2J(\text{P},\text{Te}) = 35\text{ Hz}$). MS (EI^+ , m/z), 730 $[\text{M}+\text{H}]^+$. CHN Anal.: calcd (%) for $\text{C}_{16}\text{H}_{36}\text{N}_4\text{P}_2\text{Te}_3$: C 26.35, H 4.98, N 7.68, found: C 26.34, H 4.93, N 7.63.

[Li(tmeda)]₂5: $[\text{Li}(\text{tmeda})_2][^t\text{BuN}(\text{Te})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{Te})\text{N}^t\text{Bu}]$ (0.500 g, 0.59 mmol) was suspended in toluene and cooled to $-78\text{ }^{\circ}\text{C}$. A solution of I_2 (0.075 g, 0.29 mmol) in toluene (15 mL) maintained at $-78\text{ }^{\circ}\text{C}$ was added dropwise over 15 min by cannula. The reaction mixture was stirred at that temperature for 30 min and then warmed to room temperature and stirred for an additional 1 h. Then the mixture was filtered to remove released Te and the toluene was removed under vacuum. The solid residue was dissolved in hexane, filtered and hexane was removed to afford a dark reddish black material. Recrystallisation from hexane afforded black crystals that were filtered off and dried under vacuum and identified as **[Li(tmeda)]₂5** by XRD (**estimated yield 13 % by NMR**). ^{31}P NMR (109.37 d_8 -toluene, $25\text{ }^{\circ}\text{C}$): $\delta = -78.4$ (s, $^1J(\text{P},\text{Te}) = ??$ signal too weak), -116.7 (s, $^1J(\text{P},\text{Te}) = ??$ signal too weak). **What about P-P coupling?**

§ Crystal data for [Na(tmeda)]₂**3**: C₂₈H₆₈N₈P₂Te₂Na₂, $M = 880.02$, monoclinic, space group $P21/n$, $a = 11.1830(5)$, $b = 30.2640(12)$, $c = 12.5750(5)$ Å, $\alpha = \gamma = 90.00$, $\beta = 95.151(1)^\circ$, $V = 4238.7(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.379$ g cm⁻³, $\mu = 1.500$ mm⁻¹, $T = 173(2)$ K, 12267 reflections collected (θ range 1.4–27.5°), 7193 unique ($R_{\text{int}} = 0.0436$), $R_1 = 0.0644$ for 6017 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1771$ (for all data).

Crystal data for **4**: C₁₆H₃₆N₄P₂Te₃, $M = 729.23$, monoclinic, space group $C2/c$, $a = 33.1490(2)$, $b = 14.2630(3)$, $c = 11.5420(3)$ Å, $\alpha = \gamma = 90.00$, $\beta = 107.354(1)^\circ$, $V = 5208.7(2)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.860$ g cm⁻³, $\mu = 3.469$ mm⁻¹, $T = 173(2)$ K, 20105 reflections collected (θ range 1.6–27.4°), 5894 unique ($R_{\text{int}} = 0.0408$), $R_1 = 0.0358$ for 5360 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0742$ (for all data).

Crystal data for [Li(tmeda)]₂**5**: C₅₀H₁₁₀N₁₂Li₂P₄Te₄, $M = 1818.12$, triclinic, space group $P-1$, $a = 13.760(3)$, $b = 14.301(3)$, $c = 14.481(3)$ Å, $\alpha = 60.533(5)$, $\gamma = 65.043(5)$, $\beta = 69.151(5)^\circ$, $V = 2209.3(7)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.366$ g cm⁻³, $\mu = 1.423$ mm⁻¹, $T = 93$ K, 14563 reflections collected (θ range 3.04–25.37°), 7868 unique ($R_{\text{int}} = 0.0517$), $R_1 = 0.0424$ for 5839 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1182$ (for all data).

Data for [Na(tmeda)]₂**3** and **4** were collected with a Nonius Kappa CCD diffractometer with use of monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 173 K. The structures were solved by direct methods using the program SHELXS-97²⁹ and refined with SHELXL-97³⁵ and by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were included in calculated positions and were refined by riding model. In [Na(tmeda)]₂**3**, one of the *tert*-butyl group having

carbon atom (C11) was disordered over two positions which were fixed. Data for [Li(tmeda)]₂**5** were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F² by using the program SHELXL. (Insert refs??) Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

- 1 T. Chivers and I. Manners “*Inorganic Rings and Polymers of the p-Block Elements: From Fundamentals to Applications*”, RSC Publishing, Cambridge, UK, 2009, pp. 255-260.
- 2 D. B. Sowerby in “*The Chemistry of Inorganic Homo- and Hetero-cycles*”, Ed. I. Haiduc and D. B. Sowerby, Vol. 2, Academic Press, London, UK, 1987, pp. 681-700.
- 3 G. Hua and J. D. Woollins in “*Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials*”, Ed. J. D. Woollins and R. S. Laitinen, Springer-Verlag, Heidelberg, 2011, pp. 1-39.
- 4 W.-W. du Mont, T. Severengiz and B. Meyer, *Angew. Chem., Int. Ed.*, 1983, **22**, 983.
- 5 W.-W. du Mont and T. Severengiz, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1083.

- 6 S. Grimm, K. Kariaghiosoff, P. Mayer and D. Ross, *Phosphorus, Sulfur and Silicon* 2001, **169**, 51.
- 7 K. Lux, O. Schön and K. Kariaghiosoff, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2465.
- 8 N. Nagahora, T. Sasamori and N. Tokitoh, *Heteroatom Chem.*, 2008, **19**, 443.
- 9 The six-membered ring (RPTe)₃ (R = CPh₃) is referred to in ref. 7, but no details of the characterization have been published
- 10 (a) G. G. Briand, T. Chivers and M. Parvez, *Angew. Chem. Int. Ed.*, 2002, **41**, 3468; (b) G. G. Briand, T. Chivers, M. Parvez, and G. Schatte, *Inorg. Chem.*, 2003, **42**, 525.
- 11 (a) B. Bildstein and F. Sladky, *Phosphorus, Sulfur and Silicon*, 1990, **47**, 341; (b) R. P. Davies, M. G. Martinelli, A. E. H. Wheatley, A. J. P. White and D. J. Williams, *Eur. J. Inorg. Chem.*, **2003**, 3409.
- 12 C. Rotter, M. Schuster and K. Kariaghiosoff, *Inorg. Chem.*, 2009, **48**, 7531.
- 13 (a) T. Chivers, D. J. Eisler, J. S. Ritch and H. M. Tuononen, *Angew. Chem. Int. Ed.*, 2005, **44**, 4953; (b) J. S. Ritch, T. Chivers, D. J. Eisler and H. M. Tuononen, *Chem. Eur. J.*, 2007, **13**, 4643.
- 14 For a review, see T. Chivers, J. S. Ritch, S. D. Robertson, J. Konu and H. M. Tuononen, *Acc. Chem. Res.*, 2010, **43**, 1053.
- 15 (a) J. Konu, T. Chivers and H. M. Tuononen, *Chem. Commun.*, 2006, 1634; (b) J. Konu, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2006, **45**, 10678.
- 16 A. Nordheider, T. Chivers, R. Thirumoorathi, I. Vargas-Baca and J. D. Woollins, *Angew. Chem.*, submitted (and unpublished observations).

- 17 The new reagent $[\text{Na}_2\{\text{t}^i\text{BuNP}(\mu\text{-N}^i\text{Bu})_2\text{PN}^i\text{Bu}\}]_2$ was shown to be a dimer by a single-crystal X-ray structural determination (see details in SI)
- 18 The sulfur and selenium analogues of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$, in which tmeda is replaced by two thf ligands on the Na sites, adopt a similar symmetrical bonding arrangement. (a) T. Chivers, M. Krahn, and M. Parvez, *Chem. Commun.*, 2000, 463; (b) T. Chivers, M. Krahn, M. Parvez and G. Shatte, *Inorg. Chem.*, 2001, **40**, 2547.
- 19 M. Saito, H. Hashimoto and T. Tajima, *Acta Crystallogr. Section E*, 2010, **E66**, m885.
- 20 F. Sladky, B. Bildstein, C. Rieker, A. Gieren, H. Betz and T. Hübner, *J. Chem. Soc., Chem. Commun.*, 1985, 1800
- 21 T. A. Hamor, N. Al-Salim, A. A. West and W. R. McWhinnie, *J. Organomet. Chem.*, 1986, **310**, C5.
- 22 J. Beckmann, J. Bolsingerand and A. Duthie, *Organometallics*, 2009, **28**, 4610.
- 23 N. Kuhn, H. Schumann and R. Boese, *J. Chem. Soc., Chem. Commun.*, 1987, 1257.
- 24 A P-Te bond distance of 2.605(1) Å with $^1J(\text{P},\text{Te}) = 780$ Hz has been reported for the tricyclohexylphosphine adduct of a 1,2,5-telluradiazolium cation. J. L. Dutton and P. J. Ragona, *Inorg. Chem.*, 2009, **48**, 1722.
- 25 (a) G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr.*, 1972, **B28**, 2438; (b) M. Soirlet, G. Van den Bossche. O. Dideberg and L. Dupont, *Acta Crystallogr.*, 1979, **B35**, 1727; (c) E. S. Lang, R. A. Burrow and E. T. Silveira, *Acta Crystallogr.*, 2002, **C58**, o397.

- 26 (a) S.C. Menon, H. B. Singh, J. M. Jasinski, J. P. Jasinski and R. J. Butcher, *Organometallics*, 1996, **15**, 1707; (b) J. E. Drake, M. B. Hursthouse, M. Kulcsar, M. E. Light and A. Silvestru, *J. Organomet. Chem.*, 2001, **623**, 153; (c) G. Mugesh, A. Panda, S. Kumar, S. Apte, H. B. Singh and R. Butcher, *Organometallics*, 2002, **21**, 884.
- 27 T. M. Klapotke, B. Krumm, H. Nöth, J. C. Gálvez-Ruiz, K. Polborn, I. Schwab and M. Suter, *Inorg. Chem.*, 2005, **44**, 5254.
- 28 The acute <C–Te–Te angle of 85.8(1) ° for this derivative is strongly suggestive of a significant intramolecular N···Te interaction, but this parameter is not discussed in the paper. T. Junk, K. J. Irgolic and E. A. Meyers, *Acta Crystallogr.*, 1993, **C49**, 975.
- 29 The planarity of this derivative is attributed to intramolecular nonbonded interactions between the carbonyl oxygen atoms (rather than the methoxy oxygen atoms) and the tellurium atoms. O. Niyomura, S. Kato and S. Inagaki, *J. Am. Chem. Soc.* 2000, **122**, 2132.
- 30 N. W. Alcock, *Adv. Inorg. Chem Radiochem.*, 1972, **15**, 1.
- 31 Red (?) crystals of **6** were obtained from the decomposition of [Li(tmeda)]₂**5** and identified by an X-ray structural determination [$d(\text{Te}-\text{Te}) = ??? \text{ \AA}$, $\text{P}-\text{Te}-\text{Te}-\text{P} = ???^\circ$].
- Perhaps we should include this structure in the SI (or even as Fig. 3(b) to provide a direct comparison with 5)?**
- 32 L. Lochmann, J. Pospisil and D. Li, *Tetrahedron Lett.*, 1966, **7**, 257.
- 33 I. Schanz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493.
- 34 O. Foss and W. Johannessen, *Acta Chem. Scand.*, 1961, **15** (9), 1940.
- 35 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

Captions for Figures

Fig. 1 Molecular structure of $[\text{Na}(\text{tmeda})]_2\mathbf{3}$. *tert*-Butyl groups and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): P1–Te1 2.418(2), P2–Te2 2.422(2), Na1–Te1 3.047(4), Na2–Te2 3.049(3), Na–N (range) 2.451(8)–2.750(9), P1–N3 1.576(7), P2–N4 1.566(7), P–N_{bridging}(range) 1.697(7)–1.719(7); P1–Te1–Na2 80.41(8), P2–Te2–Na2 80.35(8), Te1–Na2–Te2 125.1 (1), N3–Na1–N4 101.2(2), N5–Na1–N6 72.6(3), N7–Na2–N8 76.5(3).

Fig. 2. Molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level. Selected bond distances (Å) and angles (°): P1–Te1 2.5317(10), P2–Te2 2.5405(10), Te1–Te3 2.7155(4), Te2–Te3 2.7158(4), P1–N1 1.508(3), P2–N4 1.507(4), P–N_{bridging} 1.679(3)–1.694(3); P1–Te1–Te3 95.63(2), P2–Te2–Te3 96.06(3), Te1–Te3–Te2 104.50(1).

Fig. 3. Molecular structure of $[\text{Li}(\text{tmeda})]_2\mathbf{5}$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level. Selected bond distances (Å) and angles (°): Te1–P4 2.494(3), Te2–P3 2.379(3), Te1–Te1' 2.755(3), N6–

Li2 1.99(3), Te2–Li2 2.80(3), P4–N3 1.507(12), P3–N6 1.571(10), P–N_{bridging}(range)
1.679(9)-1.703(11), N5–Li2 2.14(3); P4–Te1–Te1' 104.75(11).

(I have pruned this list to include only the most relevant parameters – please check for
accuracy and any important omissions)

QuickTime™ and a
decompressor
are needed to see this picture.

Fig. 1

QuickTime™ and a
decompressor
are needed to see this picture.

Fig 2

QuickTime™ and a decompressor are needed to see this picture.

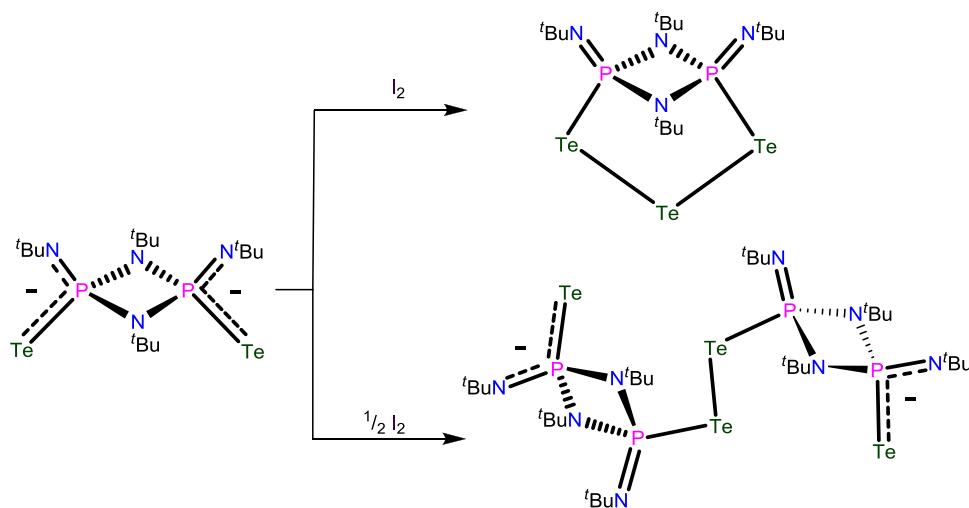
Fig 3

TOC entry

A cyclic tritelluride and a planar dianionic ditelluride supported by P_2N_2 rings

Andreas Nordheider,^{a,b} Tristram Chivers,^{a*} Ramalingam Thirumoorthi,^a Alexandra M. Z. Slawin^b and J. Derek Woollins^b

The initial oxidation of a ditelluro P_2N_2 -bridged dianion produces a dianionic ditelluride and, subsequently, a neutral tritelluride in which the $-Te-Te-Te-$ unit bridges a P_2N_2 ring



Supplementary Information

A cyclic tritelluride and a planar dianionic ditelluride supported by P_2N_2 rings[†]

Andreas Nordheider, Tristram Chivers,* Ramalingam Thirumoorthi and J. Derek Woollins

Table S1. Crystallographic data for $[\text{Na}_4\{\text{P}_2\{\mu\text{-N}^t\text{Bu}\}_2\{\text{N}^t\text{Bu}\}_2\}_2]$

	$[\text{Na}_4\{\text{P}_2\{\mu\text{-N}^t\text{Bu}\}_2\{\text{N}^t\text{Bu}\}_2\}_2]$
Empirical formula	C76 H172 N16 P8 Na8
Formula weight	1741.98
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P 21/n
a (Å), alpha (deg)	21.710(4), 90
b (Å), beta (deg)	21.271(4), 106.51(3)
c (Å), gamma (deg)	22.414(5), 90
Volume (Å ³)	9924(3)
Z	4
Calculated density (mg/m ³)	1.166
Absorption coefficient (mm ⁻¹)	0.222
F(000)	3792
Crystal size (mm ³)	0.27 x 0.16 x 0.08
Theta range (deg.)	1.4 to 27.50
Limiting indices	-21<=h<=21, -21<=k<=21, - 22<=l<=22
Reflections collected/unique	19356 / 10561 [R(int) = 0.0771]
Completeness to theta	99.0 %
Max. and min. transmission	0.9825 and 0.9425
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10561 / 0 / 897
Goodness-of-fit on F ²	1.048
R1, wR2 [I>2sigma(I)]	0.0982, 0.2610
R1, wR2 (all data)	0.1321, 0.2869
Largest diff. peak and hole (e.Å ⁻³)	0.578 and -0.459

QuickTime™ and a
decompressor
are needed to see this picture.

Figure S1.

Molecular structure of $[\text{Na}_4\{\text{P}_2\{\mu\text{-N-}i\text{Bu}\}_2\{\text{N-}i\text{Bu}\}_2\}_2]$. Bond lengths (Å): Na1–N4 2.350(8), Na1–N8 2.351(8), Na1–N1 2.802(7), Na1–N6 2.848(7), Na1–P2 3.172(4), Na1–P4 3.208(4), Na2–N7 2.347(7), Na2–N4 2.349(7), Na2–N2 2.767(7), Na2–N6 2.860(8), Na2–P2 3.167(4), Na2–P3 3.204(4), Na3–N3 2.303(8), Na3–N7 2.310(7), Na3–N5 2.886(8), Na3–N2 2.962(7), Na3–P3 3.194(4), Na3–P1 3.240(4), Na4–N8 2.312(8), Na4–N3 2.336(8), Na4–N5 2.833(8), Na4–N1 2.960(8), Na4–P4 3.167(4), Na4–P1 3.224(5), Na5–N16 2.316(8), Na5–N11 2.328(7), Na5–N14 2.848(8), Na5–N9 2.863(7), Na5–P7 3.154(4), Na5–P6 3.174(4), Na6–N16 2.337(8), Na6–N12 2.343(7), Na6–N9 2.903(7), Na6–N13 3.018(7), Na6–P5 3.217(4), Na6–P7 3.295(4), Na7–N15 2.335(7), Na7–N12 2.344(7), Na7–N10 2.762(7), Na7–N13 2.807(7), Na7–P5 3.166(4), Na7–P8 3.167(4), Na8–N11 2.317(7), Na8–N15 2.326(8), Na8–N14 2.914(7), Na8–N10 3.044(7), Na8–P8 3.215(4), Na8–P6 3.283(4), P1–N3 1.636(8), P1–N2 1.768(7), P1–N1 1.792(7), P2–N4 1.640(7), P2–N2 1.791(6), P2–N1 1.793(7), P3–N7 1.651(7), P3–N5 1.795(7), P3–N6 1.799(6), P4–N8 1.630(7), P4–N5 1.795(7), P4–N6 1.801(7), P5–N12 1.648(6), P5–N10 1.784(6), P5–N9 1.795(7), P6–N11 1.645(7), P6–N10 1.790(6), P6–N9 1.799(6), P7–N16 1.626(7), P7–N13 1.788(7), P7–N14 1.801(7), P8–N15 1.645(7), P8–N14 1.788(7), P8–N13 1.794(7), N1–C1 1.512(10), N2–C5 1.498(11) C45–C48 1.508(12), N3–C13 1.497(12) C45–C46 1.534(13), N4–C9 1.497(10) C45–C47 1.535(11), N5–C17

1.516(10), N6–C21 1.506(10), N7–C29 1.493(10), N8–C25 1.509(11), N9–C33 1.496(10), N10–C37 1.507(10), N11–C41 1.488(10), N12–C45 1.501(10), N13–C49 1.511(11), N14–C53 1.500(11) C49–C50 1.522(13), N15–C57 1.491(11) C49–C52 1.536(13), N16–C61 1.529(12) C49–C51 1.545(15), C1–C3 1.509(14), C1–C4 1.511(13), C1–C2 1.528(14), C13–C14 1.511(15), C13–C15 1.559(16), C13–C16 1.56(2), C13–C16A 1.62(3), C17–C19 1.516(13), C17–C20 1.527(13), C17–C18 1.533(14), C21–C24 1.522(12), C21–C23 1.530(14), C21–C22 1.538(13), C25–C26 1.515(16), C25–C28 1.52(2), C25–C27 1.55(2), C25–C27A 1.71(3), C25–C28A 1.73(3), C29–C32 1.518(12), C29–C30 1.521(12), C29–C31 1.545(12), C37–C39 1.496(12), C37–C40 1.512(11), C37–C38 1.520(12), C41–C42 1.501(14), C41–C44 1.523(14), C41–C43A 1.55(2), C41–C43 1.64(2), C53–C54 1.528(13), C53–C56 1.531(15), C53–C55 1.54(3), C5–C8 1.511(13) C53–C55A 1.580(17), C5–C7 1.543(13), C5–C6 1.548(13), C57–C60 1.484(16), C57–C58 1.507(15), C57–C59A 1.58(2), C57–C59 1.64(2), C9–C10 1.494(13), C9–C11 1.524(13), C9–C12 1.542(13), C61–C64A 1.48(3), C61–C63 1.525(17), C61–C64 1.60(2), C61–C62 1.60(2), C61–C62A 1.73(4). Bond angles (°): N4–Na1–N8 155.9(3), P5–N9–P6 93.7(3), N4–Na1–N1 64.4(2), C33–N9–Na5 108.5(5), N8–Na1–N1 105.4(3), P5–N9–Na5 129.8(3), N4–Na1–N6 102.9(2), P6–N9–Na5 82.4(2), N8–Na1–N6 63.2(2), C33–N9–Na6 105.6(5), N1–Na1–N6 123.4(2), P5–N9–Na6 82.8(2), N4–Na1–Na4 113.3(2), P6–N9–Na6 132.7(3), N8–Na1–Na4 47.7(2), Na5–N9–Na6 65.42(17), N1–Na1–Na4 59.87(17) C37–N10–P5 116.6(5), N6–Na1–Na4 80.93(17), C37–N10–P6 116.8(5), N4–Na1–Na2 48.54(18), P5–N10–P6 94.4(3), N8–Na1–Na2 110.2(2), C37–N10–Na7 108.0(4), N1–Na1–Na2 81.50(17), P5–N10–Na7 85.4(2), N6–Na1–Na2 57.17(16), P6–N10–Na7 129.3(3), Na4–Na1–Na2 89.16(13), C37–N10–Na8 104.7(4), N4–Na1–P2 30.13(17), P5–N10–Na8 135.2(3), N8–Na1–P2 136.0(2), P6–N10–Na8 81.1(2), N1–Na1–P2 34.23(15), Na7–N10–Na8 65.22(16), N6–Na1–P2 116.72(18), C41–N11–P6 118.7(5), Na4–Na1–P2 88.29(12), C41–N11–Na8 114.7(5), Na2–Na1–P2 60.54(10), P6–N11–Na8 110.8(3), N4–Na1–P4 134.2(2), C41–N11–Na5 118.1(5), N8–Na1–P4 29.26(18), P6–N11–Na5 104.7(3), N1–Na1–P4 118.64(18), Na8–N11–Na5 84.7(2), N6–Na1–P4 33.94(15), C45–N12–P5 118.3(5), Na4–Na1–P4 60.18(11), C45–N12–Na6 117.7(5), Na2–Na1–P4 85.76(12), P5–N12–Na6 106.1(3), P2–Na1–P4 134.86(13), C45–N12–Na7 121.5(5), N7–Na2–N4 156.5(3), P5–

N12–Na7 103.6(3), N7–Na2–N2 105.6(2), Na6–N12–Na7 83.8(2), N4–Na2–N2 64.5(2), C49–N13–P7 116.3(6), N7–Na2–N6 63.7(2), C49–N13–P8 115.6(5), N4–Na2–N6 102.6(2), P7–N13–P8 94.8(3), N2–Na2–N6 123.1(2), C49–N13–Na7 109.2(5), N7–Na2–Na1 110.7(2), P7–N13–Na7 129.6(3), N4–Na2–Na1 48.58(19), P8–N13–Na7 83.9(3), N2–Na2–Na1 81.52(17), C49–N13–Na6 106.1(5), N6–Na2–Na1 56.80(16), P7–N13–Na6 82.3(3), N7–Na2–Na3 47.34(18), P8–N13–Na6 134.3(3), N4–Na2–Na3 114.6(2), Na7–N13–Na6 64.89(16), N2–Na2–Na3 59.99(16), C53–N14–P8 115.4(6), N6–Na2–Na3 81.95(17), C53–N14–P7 116.7(5), Na1–Na2–Na3 90.93(14), P8–N14–P7 94.5(3), N7–Na2–P2 136.5(2), C53–N14–Na5 110.9(5), N4–Na2–P2 30.20(17) P8–N14–Na5 129.4(3), N2–Na2–P2 34.29(14), P7–N14–Na5 82.1(3), N6–Na2–P2 116.51(18), C53–N14–Na8 105.9(5), Na1–Na2–P2 60.69(10), P8–N14–Na8 82.5(2), Na3–Na2–P2 89.16(12), P7–N14–Na8 133.6(3), N7–Na2–P3 29.81(16), Na5–N14–Na8 65.74(17), N4–Na2–P3 134.0(2), C57–N15–P8 118.7(5), N2–Na2–P3 118.68(18), C57–N15–Na8 116.1(6), N6–Na2–P3 33.93(13), P8–N15–Na8 106.8(4), Na1–Na2–P3 85.55(12), C57–N15–Na7 120.9(6), Na3–Na2–P3 60.61(10), P8–N15–Na7 104.1(3), P2–Na2–P3 134.96(14), Na8–N15–Na7 84.6(2), N3–Na3–N7 150.6(3), C61–N16–P7 118.1(5), N3–Na3–N5 103.4(3), C61–N16–Na5 119.9(6), N7–Na3–N5 63.6(2), P7–N16–Na5 104.9(3), N3–Na3–N2 61.2(2), C61–N16–Na6 113.5(6), N7–Na3–N2 100.7(2), P7–N16–Na6 111.2(4), N5–Na3–N2 119.2(2), Na5–N16–Na6 84.1(3), N3–Na3–Na4 48.3(2), C3–C1–C4 109.9(9), N7–Na3–Na4 109.4(2), C3–C1–N1 109.0(7), N5–Na3–Na4 56.17(17), C4–C1–N1 114.3(7), N2–Na3–Na4 80.87(17), C3–C1–C2 108.4(8), N3–Na3–Na2 106.0(2), C4–C1–C2 107.3(8), N7–Na3–Na2 48.35(18), N1–C1–C2 107.7(7), N5–Na3–Na2 81.79(17), N2–Na3–Na2 53.98(15), Na4–Na3–Na2 88.70(14), N3–Na3–P3 132.4(2), N7–Na3–P3 29.72(17), N5–Na3–P3 33.85(14), N2–Na3–P3 113.17(17), Na4–Na3–P3 84.44(13), Na2–Na3–P3 60.91(10), N3–Na3–P1 28.43(19), N7–Na3–P1 130.2(2), N5–Na3–P1 114.92(18), N2–Na3–P1 32.74(14), Na4–Na3–P1 60.92(11), Na2–Na3–P1 81.85(12), P3–Na3–P1 129.86(14), N8–Na4–N3 152.6(3), N8–Na4–N5 64.0(2), N3–Na4–N5 104.1(3), N2–C5–C8 110.4(7), N8–Na4–N1 101.7(3), N2–C5–C7 107.7(7), N3–Na4–N1 62.4(2), C8–C5–C7 107.2(8), N5–Na4–N1 122.3(2), N2–C5–C6 113.7(8), N8–Na4–Na1 48.8(2), C8–C5–C6 109.6(9), N3–Na4–Na1 107.5(2), C7–C5–C6 108.0(8), N5–Na4–Na1 83.03(18), N1–Na4–Na1 54.96(16), N8–Na4–Na3 112.0(2), N3–Na4–Na3

47.4(2), N5–Na4–Na3 57.82(17), N1–Na4–Na3 83.06(18), Na1–Na4–Na3 91.20(15), N8–Na4–P4 29.74(18), N3–Na4–P4 133.8(2), N5–Na4–P4 34.26(14), N1–Na4–P4 115.15(18), Na1–Na4–P4 61.51(11), Na3–Na4–P4 86.71(13), N8–Na4–P1 131.8(2), N3–Na4–P1 29.01(18), N5–Na4–P1 117.00(19), N1–Na4–P1 33.35(14), Na1–Na4–P1 83.02(13), Na3–Na4–P1 61.45(11), C10–C9–N4 109.6(7), P4–Na4–P1 132.12(15), C10–C9–C11 109.3(9), N16–Na5–N11 156.1(3), N4–C9–C11 109.2(8), N16–Na5–N14 64.3(2), C10–C9–C12 106.6(8), N11–Na5–N14 104.2(2), N4–C9–C12 115.9(7), N16–Na5–N9 104.6(3), C11–C9–C12 106.1(7), N11–Na5–N9 64.3(2), N14–Na5–N9 127.0(2), N16–Na5–Na6 48.2(2), N11–Na5–Na6 113.1(2), N14–Na5–Na6 86.66(18), N9–Na5–Na6 57.90(16), N16–Na5–Na8 113.7(2), N11–Na5–Na8 47.53(18), N14–Na5–Na8 58.15(16), N9–Na5–Na8 86.51(17), Na6–Na5–Na8 97.35(15), N16–Na5–P7 29.87(18), N11–Na5–P7 135.3(2), N14–Na5–P7 34.45(15), N9–Na5–P7 119.60(18), Na6–Na5–P7 63.41(11), Na8–Na5–P7 87.83(13), N16–Na5–P6 135.2(2), N11–Na5–P6 30.08(17), N3–C13–C14 109.2(8), N14–Na5–P6 119.06(18), N3–C13–C15 108.8(9), N9–Na5–P6 34.19(13), C14–C13–C15 108.3(10), Na6–Na5–P6 87.01(13), N3–C13–C16 114.5(10), Na8–Na5–P6 62.80(11), C14–C13–C16 99.1(12), P7–Na5–P6 135.74(15), C15–C13–C16 116.2(11), N16–Na5–Na7 78.4(2), N3–C13–C16A 112.5(11), N11–Na5–Na7 77.69(19), C14–C13–C16A 122.1(13), N14–Na5–Na7 63.67(16), C15–C13–C16A 94.2(12), N9–Na5–Na7 63.34(15), C16–C13–C16A 26.5(9), Na6–Na5–Na7 48.62(10), Na8–Na5–Na7 48.74(10), P7–Na5–Na7 68.4(1), P6–Na5–Na7 67.34(9), N16–Na6–N12 148.5(3), N16–Na6–N9 102.9(3), N12–Na6–N9 63.1(2), N16–Na6–C64 54.5(4), N12–Na6–C64 155.8(4), N9–Na6–C64 113.4(4), N16–Na6–N13 59.8(2), N12–Na6–N13 100.2(2), N9–Na6–N13 118.0(2), C19–C17–N5 109.6(7), C64–Na6–N13 102.0(4), C19–C17–C20 109.4(9), N16–Na6–Na5 47.7(2), N5–C17–C20 107.9(7), N12–Na6–Na5 107.4(2), C19–C17–C18 108.8(9), N9–Na6–Na5 56.68(16), N5–C17–C18 113.2(7), C64–Na6–Na5 86.8(4), C20–C17–C18 107.9(9), N13–Na6–Na5 77.51(17), N16–Na6–Na7 103.4(2), N12–Na6–Na7 48.12(18), N9–Na6–Na7 78.84(16), C64–Na6–Na7 155.8(4), N13–Na6–Na7 54.31(16), Na5–Na6–Na7 83.05(13), N16–Na6–P5 131.6(2), N12–Na6–P5 29.49(16), N9–Na6–P5 33.63(14), C64–Na6–P5 140.8(4), N13–Na6–P5 112.97(17), Na5–Na6–P5 84.10(12), Na7–Na6–P5 59.83(9), N16–Na6–P7 27.37(18), N12–Na6–P7 129.3(2), N9–Na6–P7 114.00(18), C64–Na6–P7 74.8(4), N13–Na6–P7

32.52(14), N6-C21-C24 109.5(7), Na5-Na6-P7 58.86(11), N6-C21-C23 108.1(7), Na7-Na6-P7 81.14(12), C24-C21-C23 109.7(8), P5-Na6-P7 129.50(13), N6-C21-C22 112.7(7), N15-Na7-N12 161.1(3), C24-C21-C22 107.4(8), N15-Na7-N10 106.9(2), C23-C21-C22 109.4(9), N12-Na7-N10 64.6(2), N15-Na7-N13 64.5(2), N12-Na7-N13 106.4(2), N10-Na7-N13 128.4(2), N15-Na7-Na6 116.5(2), N12-Na7-Na6 48.08(17), N10-Na7-Na6 84.55(17), N13-Na7-Na6 60.80(17), N15-Na7-Na8 47.56(19), N12-Na7-Na8 117.4(2), N10-Na7-Na8 61.72(16), N13-Na7-Na8 84.37(18), Na6-Na7-Na8 96.86(14), N15-Na7-P5 138.4(2), N12-Na7-P5 30.41(16), N10-Na7-P5 34.17(13), N13-Na7-P5 120.88(18), Na6-Na7-P5 61.44(10), Na8-Na7-P5 90.81(12), N8-C25-C26 109.5(8), N15-Na7-P8 30.26(17), N8-C25-C28 110.2(10), N12-Na7-P8 138.2(2), C26-C25-C28 99.6(13), N10-Na7-P8 121.58(18), N8-C25-C27 115.7(9), N13-Na7-P8 34.29(14), C26-C25-C27 100.1(12), Na6-Na7-P8 90.19(12), C28-C25-C27 119.4(12), Na8-Na7-P8 61.31(10), N8-C25-C27A 113.0(12), P5-Na7-P8 138.49(13), C26-C25-C27A 121.0(14), N15-Na7-Na5 80.2(2), C28-C25-C27A 102.0(14), N12-Na7-Na5 80.91(18), C27-C25-C27A 23.8(10), N10-Na7-Na5 64.66(15), N8-C25-C28A 106.7(11), N13-Na7-Na5 63.76(16), C26-C25-C28A 120.2(14), Na6-Na7-Na5 48.33(10), C28-C25-C28A 22.1(11), Na8-Na7-Na5 48.53(10), C27-C25-C28A 105.0(13), P5-Na7-Na5 69.52(9), C27A-C25-C28A 83.9(15), P8-Na7-Na5 68.97(10), N11-Na8-N15 147.4(3), N11-Na8-N14 102.5(3), N15-Na8-N14 62.7(2), N11-Na8-N10 60.4(2), N15-Na8-N10 98.8(2), N14-Na8-N10 117.1(2), N7-C29-C32 109.5(6), N11-Na8-Na5 47.82(19), N7-C29-C30 116.0(7), N15-Na8-Na5 106.4(2), C32-C29-C30 107.0(7), N14-Na8-Na5 56.12(17), N7-C29-C31 107.5(7), N10-Na8-Na5 77.69(16), C32-C29-C31 108.5(8), N11-Na8-Na7 102.9(2), C30-C29-C31 108.1(7), N15-Na8-Na7 47.81(19), N14-Na8-Na7 78.83(17), N10-Na8-Na7 53.06(14), Na5-Na8-Na7 82.74(13), N11-Na8-P8 130.9(2), N15-Na8-P8 29.33(17), N14-Na8-P8 33.46(15), N10-Na8-P8 111.66(16), Na5-Na8-P8 83.29(12), Na7-Na8-P8 59.79(10), N11-Na8-P6 27.93(17), N15-Na8-P6 127.9(2), N14-Na8-P6 113.70(18), N10-Na8-P6 32.58(13), Na5-Na8-P6 59.28(10), Na7-Na8-P6 80.13(11), P8-Na8-P6 128.53(13), N3-P1-N2 107.0(4), N3-P1-N1 109.0(3), N9-C33-C35 109.1(7), N2-P1-N1 80.0(3), N9-C33-C34 112.9(7), N3-P1-P2 131.1(3), C35-C33-C34 106.9(8), N2-P1-P2 42.9(2), N9-C33-C36 108.7(7), N1-P1-P2 43.1(2), C35-C33-C36 111.2(8), N3-P1-

Na4 43.8(3), C34–C33–C36 108.0(8), N2–P1–Na4 100.3(2), N1–P1–Na4 65.2(2), P2–P1–Na4 96.33(11), N3–P1–Na3 42.1(3), N2–P1–Na3 65.0(2), N1–P1–Na3 102.6(2), P2–P1–Na3 97.26(10), Na4–P1–Na3 57.63(11), N4–P2–N2 106.6(3), N4–P2–N1 107.5(3), N2–P2–N1 79.4(3), N4–P2–P1 129.6(2), N2–P2–P1 42.3(2), N1–P2–P1 43.0(2), N4–P2–Na2 46.1(2), N2–P2–Na2 60.5(2), N1–P2–Na2 98.6(2), P1–P2–Na2 91.73(10), N4–P2–Na1 46.0(2), C39–C37–N10 108.6(6), N2–P2–Na1 97.7(2), C39–C37–C40 109.2(7), N1–P2–Na1 61.5(2), N10–C37–C40 108.9(7), P1–P2–Na1 92.35(10), C39–C37–C38 108.8(8), Na2–P2–Na1 58.77(10), N10–C37–C38 113.0(6), N7–P3–N5 107.5(3), C40–C37–C38 108.4(7), N7–P3–N6 107.5(3), N5–P3–N6 80.1(3), N7–P3–P4 130.7(2), N5–P3–P4 43.0(2), N6–P3–P4 43.2(2), N7–P3–Na3 43.9(2), N5–P3–Na3 63.6(2), N6–P3–Na3 100.0(2), P4–P3–Na3 95.16(11), N7–P3–Na2 45.0(2), N5–P3–Na2 100.2(2), N6–P3–Na2 62.5(2), P4–P3–Na2 94.56(10), Na3–P3–Na2 58.49(10), N8–P4–N5 107.4(3), N8–P4–N6 106.8(3), N5–P4–N6 80.1(3), N8–P4–P3 130.1(3), N5–P4–P3 43.0(2), N11–C41–C42 108.2(7), N6–P4–P3 43.2(2), N11–C41–C44 109.4(7), N8–P4–Na4 44.7(3), C42–C41–C44 107.5(9), N5–P4–Na4 62.6(2), N11–C41–C43A 114.8(10), N6–P4–Na4 98.6(2), C42–C41–C43A 96.2(12), P3–P4–Na4 93.68(11), C44–C41–C43A 119.2(12), N8–P4–Na1 44.8(3), N11–C41–C43 113.9(9), N5–P4–Na1 100.1(2), C42–C41–C43 119.0(11), N6–P4–Na1 62.0(2), C44–C41–C43 98.1(1), P3–P4–Na1 94.13(10), C43A–C41–C43 26.1(9), Na4–P4–Na1 58.31(11), N12–P5–N10 106.4(3), N12–P5–N9 107.8(3), N10–P5–N9 80.5(3), N12–P5–P6 129.4(2), N10–P5–P6 42.9(2), N9–P5–P6 43.2(2), N12–P5–Na7 46.0(2), N10–P5–Na7 60.4(2), N9–P5–Na7 97.4(2), P6–P5–Na7 90.68(10), N12–P5–Na6 44.4(2), N10–P5–Na6 101.3(2), N12–C45–C48 107.1(6), N9–P5–Na6 63.6(2), N12–C45–C46 108.3(7), P6–P5–Na6 95.20(11), C48–C45–C46 110.2(8), Na7–P5–Na6 58.73(10), N12–C45–C47 115.6(6), N11–P6–N10 107.5(3), C48–C45–C47 108.6(8), N11–P6–N9 108.6(3), C46–C45–C47 106.9(8), N10–P6–N9 80.3(3), N11–P6–P5 130.5(2), N10–P6–P5 42.7(2), N9–P6–P5 43.1(2), N11–P6–Na5 45.2(2), N10–P6–Na5 98.7(2), N9–P6–Na5 63.4(2), P5–P6–Na5 93.62(10), N11–P6–Na8 41.3(2), N10–P6–Na8 66.3(2), N9–P6–Na8 104.1(2), P5–P6–Na8 98.34(10), Na5–P6–Na8 57.92(11), N16–P7–N13 106.4(3), N16–P7–N14 108.6(3), N13–P7–N14 79.8(3), N16–P7–P8 129.5(3), N13–P7–P8 42.7(2), N14–P7–P8 42.5(2), N13–C49–C50 108.5(8), N16–P7–Na5 45.2(3), N13–C49–C52 112.9(8), N13–P7–Na5 98.2(2), C50–

C49–C52 108.6(8), N14–P7–Na5 63.4(2), N13–C49–C51 109.2(7), P8–P7–Na5 92.99(10), C50–C49–C51 109.3(9), N16–P7–Na6 41.4(3), C52–C49–C51 108.3(9), N13–P7–Na6 65.2(2), N14–P7–Na6 103.1(2), P8–P7–Na6 96.88(10), Na5–P7–Na6 57.74(11), N15–P8–N14 107.7(3), N15–P8–N13 107.5(3), N14–P8–N13 80.0(3), N15–P8–P7 129.6(3), N14–P8–P7 42.9(2), N13–P8–P7 42.5(2), N15–P8–Na7 45.7(2), N14–P8–Na7 98.0(2), N13–P8–Na7 61.8(2), P7–P8–Na7 91.72(10), N15–P8–Na8 43.8(3), N14–P8–Na8 64.0(2), N13–P8–Na8 102.2(2), P7–P8–Na8 95.75(11), Na7–P8–Na8 58.9(1), N14–C53–C54 113.4(8), C1–N1–P1 116.1(5), N14–C53–C56 108.7(8), C1–N1–P2 116.4(5), C54–C53–C56 108.1(9), P1–N1–P2 93.9(3), N14–C53–C55 109.9(12), C1–N1–Na1 108.5(5), C54–C53–C55 122.4(13), P1–N1–Na1 130.6(3), C56–C53–C55 91.4(13), P2–N1–Na1 84.3(3), N14–C53–C55A 107.7(8), C1–N1–Na4 107.9(5), C54–C53–C55A 102.1(9), P1–N1–Na4 81.4(2), C56–C53–C55A 116.9(10), P2–N1–Na4 132.3(3), C55–C53–C55A 27.4(10), Na1–N1–Na4 65.17(17), C5–N2–P1 116.7(5), C5–N2–P2 115.7(5), P1–N2–P2 94.8(3), C5–N2–Na2 105.5(5), P1–N2–Na2 132.5(3), P2–N2–Na2 85.2(2), C5–N2–Na3 105.1(5), P1–N2–Na3 82.3(3), P2–N2–Na3 135.2(3), Na2–N2–Na3 66.02(17), C13–N3–P1 117.9(6), C13–N3–Na3 115.9(6), C60–C57–N15 109.2(9), P1–N3–Na3 109.5(4), C60–C57–C58 110.7(10), C13–N3–Na4 117.0(6), N15–C57–C58 108.6(8), P1–N3–Na4 107.2(4), C60–C57–C59A 95.6(11), Na3–N3–Na4 84.4(3), N15–C57–C59A 114.5(10), C9–N4–P2 117.6(5), C58–C57–C59A 117.4(12), C9–N4–Na2 120.4(5), C60–C57–C59 117.8(11), P2–N4–Na2 103.7(3), N15–C57–C59 112.9(9), C9–N4–Na1 122.1(5), C58–C57–C59 96.8(11), P2–N4–Na1 103.9(3), C59A–C57–C59 25.0(9), Na2–N4–Na1 82.9(2), C17–N5–P3 115.0(5), C17–N5–P4 117.8(5), P3–N5–P4 93.9(3), C17–N5–Na4 108.8(5), P3–N5–Na4 131.5(3), P4–N5–Na4 83.1(3), C17–N5–Na3 105.9(5), P3–N5–Na3 82.5(3), P4–N5–Na3 132.8(3), Na4–N5–Na3 66.00(18), C21–N6–P3 115.9(5), C21–N6–P4 116.1(5), C64A–C61–C63 124.5(16), P3–N6–P4 93.6(3), C64A–C61–N16 112.3(14), C21–N6–Na1 106.5(4), C63–C61–N16 114.1(9), P3–N6–Na1 133.4(3), C64A–C61–C64 39.2(13), P4–N6–Na1 84.0(3), C63–C61–C64 98.2(13), C21–N6–Na2 106.7(5), N16–C61–C64 106.6(10), P3–N6–Na2 83.6(2), C64A–C61–C62 72.3(16), P4–N6–Na2 133.3(3), C63–C61–C62 118.7(14), Na1–N6–Na2 66.03(17), N16–C61–C62 107.6(11), C29–N7–P3 116.6(5), C64–C61–C62 110.8(13), C29–N7–Na3 118.2(5), C64A–C61–C62A 107.(2), P3–N7–Na3

106.3(3), C63–C61–C62A 87.0(16), C29–N7–Na2 121.1(5), N16–C61–C62A 107.2(15), P3–N7–Na2 105.2(3), C64–C61–C62A 140.0(16), Na3–N7–Na2 84.3(2), C62–C61–C62A 37.6(13), C25–N8–P4 118.1(6), C25–N8–Na4 119.0(6), P4–N8–Na4 105.6(3), C25–N8–Na1 119.0(5), P4–N8–Na1 105.9(4), Na4–N8–Na1 83.5(3), C33–N9–P5 117.3(5), C61–C64–Na6 85.1(8), C33–N9–P6 117.4(5).

X-ray Crystallography

Crystallographic data for $[\text{Na}_4\{\text{P}_2\{\mu\text{-}N\text{-}t\text{Bu}\}_2\{\text{N-}t\text{Bu}\}_2\}_2]$ are given in Table 1. Data were collected with a Nonius Kappa CCD diffractometer with use of monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $-150 \text{ }^\circ\text{C}$. The structures were solved by direct methods using the program SHELXS-97¹ and refined with SHELXL-97¹ and by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were included in calculated positions and were refined by riding model. *tert*-Butyl groups having carbon atoms (C16, C27, C28, C43, C55, C59, C62, C64) were disordered over two positions which were fixed. Two disordered solvent hexane molecules in asymmetric unit were removed from the diffraction data with SQUEEZE. SQUEEZE estimated the electron count in the void is 445. This value is closely related to the eight hexane molecules (432) in cell.

1 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.