# A planar dianionic ditelluride and a cyclic tritelluride supported by $\mathbf{P}_{\mathbf{2}} \mathbf{N}_{\mathbf{2}}$ rings $\dagger$ 

Andreas Nordheider, ${ }^{\text {a,b }}$ Tristram Chivers, ${ }^{\mathrm{a}^{*}}$ Ramalingam Thirumoorthi, ${ }^{\text {a }}$ Kasun S. Athukorala Arachchige, ${ }^{\text {b }}$ Alexandra M. Z. Slawin, ${ }^{\text {b }}$ J. Derek Woollins ${ }^{\text {b }}$ and Ignacio Vargas-Baca ${ }^{\text {c }}$<br>${ }_{5}$ Received (in $\left.X X X, X X X\right)$ Xth $X X X X X X X X X ~ 20 X X$, Accepted Xth XXXXXXXXXX 20XX<br>DOI: 10.1039/b000000x

Oxidation of alkali metal derivatives of $\left[\operatorname{Te}\left({ }^{t} \operatorname{BuN}\right) P(\mu\right.$ $\left.\left.\mathbf{N}^{t} \mathbf{B u}\right)_{2} \mathbf{P}\left(\mathbf{N}^{t} \mathbf{B u}\right) \mathbf{T e}\right]^{2-}$ with $\mathbf{I}_{2}$ produces the intermediate ditelluride dianion $\left[\mathrm{Te}\left({ }^{t} \mathrm{BuN}\right) \mathbf{P}\left(\mu-\mathbf{N}^{t} \mathbf{B u}\right)_{2} \mathbf{P}\left(\mathbf{N}^{t} \mathrm{Bu}\right) \mathrm{Te}\right]_{2}{ }^{2-}$ with a ${ }_{10}$ planar PTeTeP conformation and, subsequently, the cyclic tritelluride $\left[\left({ }^{t} \mathbf{B u N}\right) \mathbf{P}\left(\mu-\mathbf{N}^{t} \mathbf{B u}\right){ }_{2} \mathbf{P}\left(\mathbf{N}^{t} \mathbf{B u}\right)(\mu-\mathrm{TeTeTe})\right]$.

In their pioneering studies of inorganic macrocycles that incorporate $\mathrm{P}_{2} \mathrm{~N}_{2}$ rings, ${ }^{1}$ Wright and co-workers have employed cyclocondensation to generate NH - or O-bridged systems of ${ }_{15}$ various sizes involving $\mathrm{P}^{\mathrm{II}}{ }_{2} \mathrm{~N}_{2}$ rings ${ }^{2,3}$ and a reductive method for the synthesis of a hexamer in which monoselenido ( $-\mathrm{Se}-$ ) units span $\mathrm{P}^{\text {III }} \mathrm{P}^{\mathrm{V}} \mathrm{N}_{2}$ rings. ${ }^{4}$ Recently, we have applied a mild oxidative approach to generate the trimers $\left[{ }^{t} \mathrm{BuN}\right) \mathrm{P}\left(\mu-\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right)(\mu-\mathrm{E}-$ $\mathrm{E}-)]_{3}$ with a planar $\mathrm{P}_{6} \mathrm{E}_{6}(\mathrm{E}=\mathrm{S}$, Se$)$ framework in which 20 dichalcogenido ( $-\mathrm{E}-\mathrm{E}-$ ) groups are linked by perpendicular $\mathrm{P}^{\mathrm{V}}{ }_{2} \mathrm{~N}_{2}$ rings. ${ }^{5}$ The synthesis of these polychalcogen macrocycles involves the two-electron oxidation of the dianions $\mathbf{1 a}$ and $\mathbf{1 b}$ with $\mathrm{I}_{2}$. We now report a detailed investigation of the oxidation of the tellurium analogue $\mathbf{1 c}$ that provides important insights into the ${ }_{25}$ initial oxidation process, as well as a notable difference in the final outcome of the oxidation compared to that observed for 1a and 1b. Specifically, we have identified and structurally characterised (a) the dianionic ditelluride $\left[\mathrm{Te}\left({ }^{\mathrm{t}} \mathrm{BuN}\right) \mathrm{P}(\mu\right.$ $\left.\left.\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right) \mathrm{Te}\right]_{2}{ }^{2-}(\mathbf{2})$, with an unusual planar conformation, as ${ }_{30}$ the product of one-electron oxidation of $\mathbf{1 c}$ and (b) the cyclic tritelluride $\left[\left({ }^{t} \mathrm{BuN}\right) \mathrm{P}\left(\mu-\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right)(\mu-\mathrm{TeTeTe})\right]$ (3) as the result of further oxidation. DFT calculations were carried out in order to determine the reason(s) for the unusual planarity of the PTeTeP unit in the ditelluride 2.
${ }_{35}$ The oxidation of the dianion $\mathbf{1 c}$ (as its dilithium derivative) ${ }^{6 \mathrm{a}}$ with a one-half molar equivalent of $\mathrm{I}_{2}$ led to the isolation of extremely sensitive black crystals, which were identified by Xray crystallography as $[\mathrm{Li}(\text { tmeda })]_{2} 2$ (Eq. 1). ${ }^{7}$ As depicted in Fig. 1, the dianion $\left[\mathrm{Te}\left({ }^{t} \mathrm{BuN}\right) \mathrm{P}\left(\mu-\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right) \mathrm{Te}\right]_{2}{ }^{2-}$ (2) is ${ }_{40}$ comprised of a central ditellurido unit that links two $\mathrm{P}^{\mathrm{V}}{ }_{2} \mathrm{~N}_{2}$ rings, each of which has exocyclic Te and $\mathrm{N}^{t} \mathrm{Bu}$ substituents that are $N, T e-$ chelated to the tmeda-solvated $\mathrm{Li}^{+}$counterions. The ${ }^{31} \mathrm{P}$ NMR spectrum of $[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2}$ in $\mathrm{d}_{8}$-toluene exhibits singlets at $\delta=-78.5$ and -117.0 with ${ }^{1} J(\mathrm{P}, \mathrm{Te})=1670$ and 1219 Hz , ${ }_{45}$ respectively, reflecting the disparity in the $\mathrm{P}-\mathrm{Te}$ bond lengths $[\mathrm{d}(\mathrm{P} 2-\mathrm{Te} 2)=2.396(2)$ and $\mathrm{d}(\mathrm{P} 1-\mathrm{Te} 1)=2.497(2) \AA]$. The $\mathrm{Te} 1-$ Te1' bond length in 2 is $2.777(3) \AA$, cf. 2.70-2.71 $\AA$ for typical aryl ditellurides, ${ }^{8} 2.75-2.76 \AA$ for ditellurides supported by an intramolecular $\mathrm{Te} \cdots \mathrm{N}$ interaction, ${ }^{9}$ and $2.77 \AA$ for the bulky ${ }_{50}$ derivative $(\mathrm{TpsiTe})_{2}\left(\mathrm{Tpsi}=\operatorname{tris}\left(\right.\right.$ phenyldimethylsilyl)methyl. ${ }^{10}$

$\mathbf{1 a}(E=S), \mathbf{1 b}(E=S e)$
2 1c ( $\mathrm{E}=\mathrm{Te}$ )
Atypically, the ditelluride $[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2}$ is perfectly planar (< $\mathrm{P}-\mathrm{Te}-\mathrm{Te}-\mathrm{P}=180.0^{\circ}$ ). The only other examples of antiperiplanar ditellurides are bis(chloro-2-pyridyl) ditelluride ${ }^{11}$ and the diacyl ${ }_{55}$ ditelluride $\left(2-\mathrm{MeOC}_{6} \mathrm{H}_{4} \mathrm{COTe}\right)_{2}$, ${ }^{12}$ which exhibit intramolecular heteroatom-tellurium interactions and $(\mathrm{TpsiTe})_{2}$ for which the antiperiplanar conformation is imposed by the bulky substituents. ${ }^{10}$ The $\mathrm{Te} 1 \cdots \mathrm{Te} 2$ ' distance in $\left[\mathrm{Li}(\text { tmeda) }]_{2} \mathbf{2}\right.$ $(3.884 \AA)$ is shorter than the sum of van der Waals radii for Te $60(4.12 \AA) .{ }^{13}$ Moreover, the closely related neutral ditelluride $\left[\left({ }^{t} \mathrm{BuNH}\right) \mathrm{P}\left(\mu-\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right) \mathrm{Te}\right]_{2}$ (4), which has a similar steric environment for the $\mathrm{Te}-\mathrm{Te}$ linkage, exhibits a dihedral angle of $-123.8^{\circ}$ and a $\mathrm{Te}-\mathrm{Te}$ bond length of 2.7204(9) $\AA$ (Fig. S1). ${ }^{14}$ In view of these observations, DFT calculations were carried out to ${ }_{65}$ probe whether the conformation of $[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2}$ is stabilized by intramolecular $\mathrm{Te} 1 \cdots \mathrm{Te} 2$ ' secondary bonding interactions ( $3.884 \AA$ A) . Satisfactory structures were obtained from geometry optimizations (PBE-D3, TZP, ZORA) for planar and synclinal models of $[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2}$ and $\mathbf{4}$ simplified using Me groups in lieu 70 of ${ }^{t} \mathrm{Bu}$. In both instances the planar conformations were higher in energy, by 8 and $37 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for the models of $\left[\mathrm{Li}(\text { tmeda }]_{2} \mathbf{2}\right.$ and 4, respectively. Preferred $\mathrm{P}-\mathrm{Te}-\mathrm{Te}-\mathrm{P}$ torsion angles are $98^{\circ}$ for the former and $90^{\circ}$ for the latter. The small difference of energy suggests that the conformation observed in the crystal structure of
${ }_{75}[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2}$ is imposed by packing forces. Further analysis on the electronic structures of the $[\mathrm{Li}(\text { tmeda })]_{2} 2$ models failed to identify a particular orbital interaction or contribution from dispersion that would help stabilize the antiperiplanar geometry.

$$
\begin{equation*}
{ }^{80} 2[\mathrm{Li}(\text { tmeda })]_{2} 1 \mathbf{c} \xrightarrow[-2 \mathrm{Lil}]{\mathrm{I}_{2}}[\mathrm{Li}(\text { tmeda })]_{2} \mathbf{2} \tag{1}
\end{equation*}
$$

In order to provide a direct comparison of the oxidation of $\mathbf{1 c}$ with that of $\mathbf{1 a}$ and $\mathbf{1 b}^{5}$, we have developed a synthesis of the sodium salt $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}$ via the metallation-telluration sequence illustrated in Scheme 1. Yellow crystals of


Scheme 1 Synthesis of the cyclic tritelluride 3
$[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}$ suitable for an X-ray analysis were obtained from $n$-hexane at $-30^{\circ} \mathrm{C}$ and the molecular structure is illustrated in Fig. 2. ${ }^{15}$ In contrast to the lithium analogue $[\mathrm{Li}(\mathrm{thf})]_{2} \mathbf{1 c}$ in which 10 the dianionic ligand is coordinated to the $\mathrm{Li}^{+}$cations asymmetrically ( $T e, T e^{\prime}$ and $N, T e$ chelation), ${ }^{6 a}$ the sodium salt $\left[\mathrm{Na}(\text { tmeda) }]_{2} \mathbf{1 c}\right.$ adopts a symmetrical structure ( $T e, T e^{\prime}$ and $N, N^{\prime}$ coordination). ${ }^{17}$ The mean $\mathrm{P}-\mathrm{Te}$ distance of $2.420(2) \AA$ in $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1} \mathbf{c}$ is shorter by ca. $0.03 \AA$ than that involving the 15 two-coordinate Te in $[\mathrm{Li}(\mathrm{thf})]_{2} \mathbf{1} \mathbf{c} .{ }^{6 a}$ Consistently, the ${ }^{1} J(\mathrm{P}, \mathrm{Te})$ coupling constant of 1583 Hz for $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}$ is substantially larger than the values of 1309 and 1467 Hz found for the lithium analogue. ${ }^{6 \mathrm{a}}$ A doublet is observed in the ${ }^{125} \mathrm{Te}$ NMR spectrum of $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}$ at -148.7 ppm , cf. -289 and -87 ppm for the ${ }_{20}$ inequivalent Te environments in $[\mathrm{Li}(\mathrm{thf})]_{2} \mathbf{1} \mathbf{c}{ }^{6 \mathrm{a}}$


Fig. 1. Molecular structure of $[\mathrm{Li}(\text { tmeda })]_{2}$ 2. Hydrogen atoms have been omitted for clarity. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right): \mathrm{Te} 1-\mathrm{Te} 1^{\prime}$ 25 2.7768(8), Te1-P1 2.4970(18), Te2-P2 2.3957(18), N4-Li1 2.008(9), Te2-Li1 2.848(12), P1-N1 1.510(6), P2-N4 1.566(5), P-N $\mathrm{N}_{\text {bridging }}($ range $)$ 1.679(4)-1.712(4), N5-Li1 2.171(9), P1-Te1-Te1' 104.41(4).

Treatment of $[\mathrm{Na}(\mathrm{tmeda})]_{2} \mathbf{1} \mathbf{c}$ with an equimolar quantity of $\mathrm{I}_{2}$ in toluene produced a dark red-black solid, which was ${ }_{30}$ recrystallised from pentane to give black crystals that were identified as the tritelluride $\left[\left({ }^{t} \mathrm{BuN}\right) \mathrm{P}\left(\mu-\mathrm{N}^{t} \mathrm{Bu}\right)_{2} \mathrm{P}\left(\mathrm{N}^{t} \mathrm{Bu}\right)(\mu\right.$ TeTeTe )] (3) by single-crystal X-ray analysis. ${ }^{18}$ Higher yields (41\%) of $\mathbf{3}$ are obtained via metathesis of $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1} \mathbf{c}$ with $\mathrm{TeCl}_{2} \cdot$ tmtu in toluene (Scheme 1).
${ }_{35}$ As shown in Fig. 3, the molecular structure of $\mathbf{3}$ is comprised of a tritelluride ligand bridging the $\mathrm{P}^{\mathrm{V}} \mathrm{N}_{2}$ ring. Compound $\mathbf{3}$ is a rare example of a cyclic tritelluride, the only other representative being the $\mathrm{Sn}^{\mathrm{IV}}$ complex $\left[\mathrm{ArSn}(\mu-\mathrm{Te})_{2}(\mu-\mathrm{TeTeTe}) \mathrm{SnAr}\right](\mathrm{Ar}=2,6-$ bis(2,4,6-triisopropylphenyl)phenyl). ${ }^{19}$ Structurally characterised


Fig. 2. Molecular structure of $[\mathrm{Na}(\mathrm{tmeda})]_{2} \mathbf{1 c}$. tert-Butyl groups and hydrogen atoms have been omitted for clarity. Selected bond distances (A) and angles ( ${ }^{\circ}$ ): 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 45 1.576(7), P2-N4 1.566(7), P-N ${ }_{\text {bridging }}$ (range) 1.697(7)-1.719(7); P1-Te1Na2 80.41(8), P2-Te2-Na2 80.35(8), Te1-Na2-Te2 125.1 (1), N3-Na1N4 101.2(2), N5-Na1-N6 72.6(3), N7-Na2-N8 76.5(3).


Fig. 3. Molecular structure of 3. Hydrogen atoms have been omitted for 50 clarity. Selected bond distances ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ : P1-Te1 2.5317(10), P2-Te2 2.5405(10), Te1-Te3 2.7155(4), Te2-Te3 2.7158(4), P1-N1 $1.508(3), \mathrm{P} 2-\mathrm{N} 41.507(4), \mathrm{P}-\mathrm{N}_{\text {bridging }} 1.679(3)-1.694(3) ; \mathrm{P} 1-\mathrm{Te} 1-\mathrm{Te} 3$ 95.63(2), P2-Te2-Te3 96.06(3), $\mathrm{Te} 1-\mathrm{Te} 3-\mathrm{Te} 2$ 104.50(1).
acyclic tritellurides incorporate either bulky substituents ${ }_{55} \mathrm{RTeTeTeR} \quad\left(\mathrm{R}=\mathrm{C}\left(\mathrm{SiMe}_{3}\right)_{3}\right)^{20}$ or intramolecular $\mathrm{N} \cdots \mathrm{Te}$ coordination (2-pyridyl- $\mathrm{C}_{6} \mathrm{H}_{5},{ }^{21}{ }^{8}-\mathrm{Me}_{2} \mathrm{NC}_{10} \mathrm{H}_{7}{ }^{22}$ ); the thermally unstable dication $\left.{ }^{t} \mathrm{Bu}_{3} \mathrm{PTeTeTeP}^{t} \mathrm{Bu}_{3}\right]^{2+}$ has also been identified. ${ }^{23}$ The mean $\mathrm{Te}-\mathrm{Te}$ bond length of $2.716(1) \AA$ and $\mathrm{Te}-$ $\mathrm{Te}-\mathrm{Te}$ bond angle of $104.50(1)^{\circ}$ in $\mathbf{3}$ are comparable to the ${ }_{60}$ corresponding values of 2.705(2) $\AA$ and $104.02(5)^{\circ}$ found for $\left[\mathrm{ArSn}(\mu-\mathrm{Te})_{2}(\mu-\mathrm{TeTeTe}) \mathrm{SnAr}\right] .{ }^{19}$ The $\mathrm{P}-\mathrm{Te}$ bond length of $2.536(1) \AA$ is notably longer (by ca. $0.12 \AA$ ) than the mean value for $[\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}$ indicating a weak $\mathrm{P}-\mathrm{Te}$ bond in $\mathbf{3}$. Consistently, the ${ }^{1} J(\mathrm{P}, \mathrm{Te})$ coupling of 1030 Hz observed in both
the ${ }^{31} \mathrm{P}$ and ${ }^{125} \mathrm{Te}$ NMR spectra of $\mathbf{3}$ in $d_{8}$-toluene is among the lowest reported for $\mathrm{P}-\mathrm{Te}$ compounds. ${ }^{24}$ The ${ }^{125} \mathrm{Te}$ NMR spectrum of $\mathbf{3}$ is comprised of a well-separated pseudo-doublet of doublets at $-442.8 \mathrm{ppm}\left({ }^{1} J(\mathrm{P}, \mathrm{Te})=1031 \mathrm{~Hz},{ }^{3} J(\mathrm{P}, \mathrm{Te})=41 \mathrm{~Hz}\right)$, and a ${ }_{5}$ pseudo-triplet centred at $+361.9\left(\mathrm{t},{ }^{2} J(\mathrm{P}, \mathrm{Te})=35 \mathrm{~Hz}\right)$; these resonances are assigned to the equivalent pair of tellurium atoms $\mathrm{Te} 1, \mathrm{Te} 2$ and the unique tellurium centre Te 3 , respectively (Fig. 3). The heterocycle $\mathbf{3}$ is the first structurally characterised neutral $\mathrm{P}-\mathrm{Te}$ ring, although the cation $\left[\mathrm{N}\left(\mathrm{P}^{i} \mathrm{Pr}_{2} \mathrm{Te}\right)_{2}\right]^{+}$embodying a five${ }_{10}$ membered $\mathrm{NP}^{\mathrm{V}}{ }_{2} \mathrm{Te}_{2}$ ring is known. ${ }^{25}$

In summary, the formation of the ditellurido linkage in 2 is comparable to the generation of neutral dichalcogenides upon one-electron oxidation of the PNP-bridged monoanions $\left[\mathrm{EPR}_{2} \mathrm{NPR}_{2} \mathrm{PE}\right]^{-} \quad\left(\mathrm{E}=\mathrm{S}, \mathrm{Se}, \mathrm{Te} ; \mathrm{R}={ }^{i} \mathrm{Pr},{ }^{t} \mathrm{Bu}\right) .{ }^{26}$ The 15 identification of the acyclic intermediate $\mathbf{2}$ provides an important discernment into the process involved in the construction of $\mathrm{P}^{\mathrm{V}}{ }_{2} \mathrm{~N}_{2}$-bridged polychalcogen macrocycles via the oxidation pathway. ${ }^{27}$ It also supplies an incentive for investigations of the sulfur and selenium analogues, which are potentially versatile 20 building blocks for the construction of $\mathrm{P}^{\mathrm{V}}{ }_{2} \mathrm{~N}_{2}$-stabilised macrocycles that incorporate main group elements or transition metals in addition to dichalcogenido linkages.

## Notes and references

$25{ }^{a}$ 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
$30^{\text {c }}$ Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, Canada L8S 4M1
${ }^{\dagger}$ Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC references numbers 909218909222 for $\left([\mathrm{Na}(\text { tmeda })]_{2} \mathbf{1 c}\right)$, ([Li(tmeda) $\left.]_{2} \mathbf{2}\right), \mathbf{3}, 4$ and $\left[\mathrm{Na}_{4}\left(\mathrm{P}_{2}(\mu-\right.\right.$ $\left.\left.\left.{ }_{35} \mathrm{~N}^{\prime} \mathrm{Bu}\right)_{2}\left(\mathrm{~N}^{\prime} \mathrm{Bu}\right)_{2}\right)_{2}\right]$

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