

## COMMUNICATION

Sodium and rhodium complexes of a spirocyclic Te<sub>5</sub> dianion supported by P<sub>2</sub>N<sub>2</sub> rings

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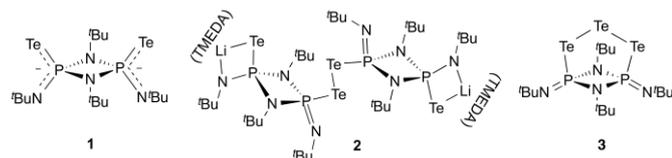
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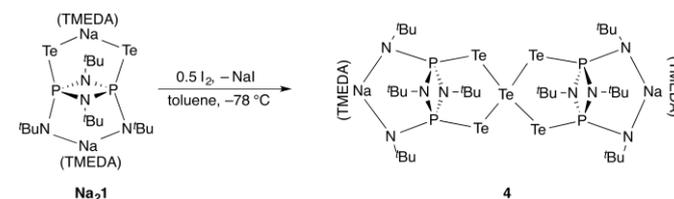
**Reactions of the dianion [Te(<sup>i</sup>BuN)P( $\mu$ -N<sup>i</sup>Bu)<sub>2</sub>P(N<sup>i</sup>Bu)Te]<sup>2-</sup> with I<sub>2</sub> or [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> unexpectedly produced complexes of the novel spirocyclic Te<sub>5</sub> dianion [Te(<sup>i</sup>BuN)P( $\mu$ -N<sup>i</sup>Bu)<sub>2</sub>P(Te)N<sup>i</sup>Bu]<sub>2</sub> $\mu$ -Te]<sup>2-</sup>, which is *N,N'*-coordinated to two Na<sup>+</sup> ions in the disodium derivative and adopts a Te,Te',Te''-bonding mode in the Cp<sup>\*</sup>Rh complex.**

The dianion [Te(<sup>i</sup>BuN)P( $\mu$ -N<sup>i</sup>Bu)<sub>2</sub>P(N<sup>i</sup>Bu)Te]<sup>2-</sup> (**1**) was first reported in 2002.<sup>1</sup> Recently we showed that the oxidation of **Li<sub>2</sub>1** with a one-half molar equivalent of I<sub>2</sub> produces the dianionic ditelluride **2**.<sup>2</sup> In addition, we reported that the major product is the cyclic tritelluride **3** when the oxidation is carried out using the disodium derivative **Na<sub>2</sub>1** and one molar equivalent of iodine.<sup>2</sup> In this communication we describe the isolation and structural characterisation of the disodium derivative of the novel, spirocyclic dianion [Te(<sup>i</sup>BuN)P( $\mu$ -N<sup>i</sup>Bu)<sub>2</sub>P(Te)N<sup>i</sup>Bu]<sub>2</sub> $\mu$ -Te]<sup>2-</sup> (**4**) when the oxidation of [Na(TMEDA)]<sub>2</sub>**1** is limited to a one-half molar equivalent of I<sub>2</sub>. Interestingly a Cp<sup>\*</sup>Rh(III) complex of the same spirocyclic dianion (**5**) is obtained from the attempted metathesis of [Li(TMEDA)]<sub>2</sub>**1** with [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub>. A comparison of the structures of **4** and **5** illustrates the potentially versatile coordination chemistry of the novel spirocyclic Te<sub>5</sub>-centred dianion.



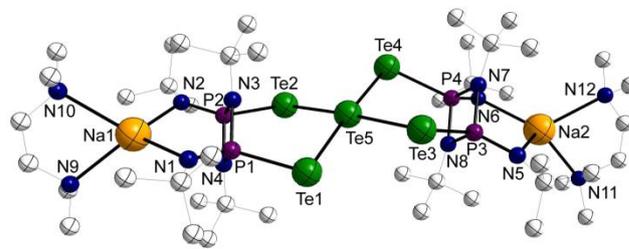
The treatment of [Na(TMEDA)]<sub>2</sub>**1** with 0.5 equivalents of iodine produced a black precipitate. This product decomposes

in THF or acetonitrile and has very limited solubility in *n*-hexane and toluene. However, a small amount of extremely air-sensitive and thermally unstable red crystals identified by a single crystal X-ray analysis as [Na(TMEDA)]<sub>2</sub>[Te(<sup>i</sup>BuN)P( $\mu$ -N<sup>i</sup>Bu)<sub>2</sub>P(Te)N<sup>i</sup>Bu]<sub>2</sub> $\mu$ -Te] (**4**) (Scheme 1) were isolated from a dilute solution in *n*-hexane after 3 days at -40 °C.<sup>3</sup>



**Scheme 1** Reaction of [Na(TMEDA)]<sub>2</sub>**1** with 0.5 eq. of I<sub>2</sub>.

As illustrated in Fig. 1, complex **4** is comprised of a dianion with a central, spirocyclic Te<sub>5</sub> motif and at the two termini it is *N,N'*-coordinated to two TMEDA-solvated Na<sup>+</sup> counter-ions. The reaction of the dianion **1** with *in situ*-generated cyclic tritelluride **3** is a possible source of this spirocyclic arrangement.



**Fig. 1** Molecular structure of **4**. Hydrogen atoms and solvate toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–P1 2.444(4), Te1–Te5 3.0268(17), Te2–Te5

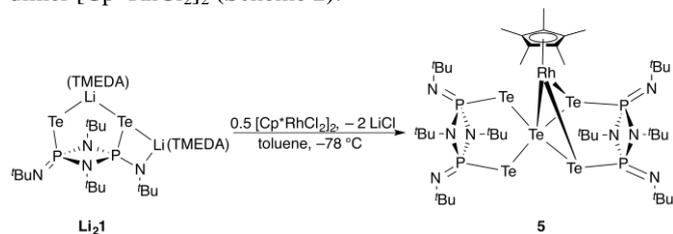
3.0258(17), Te2–P2 2.442(4), Te3–Te5 3.0152(18), Te3–P3 2.445(4), Te4–Te5 3.0144(18), Te4–P4 2.438(4); Te5–Te1–P1 95.36(10), Te5–Te2–P2 95.54(10), Te5–Te3–P3 94.99(11), Te5–Te4–P4 94.53(11), Te1–Te5–Te2 105.61(5), Te1–Te5–Te3 74.47(4), Te1–Te5–Te4 176.80(5), Te2–Te5–Te3 176.24(5), Te2–Te5–Te4 75.85(4), Te3–Te5–Te4 103.87(5).

The dianion in **4** can be viewed as a complex of  $\text{Te}^{2+}$  coordinated to two  $\text{Te}, \text{Te}'$ -chelating dianions **1**. The central  $\text{Te}_5$  motif has several structurally characterised precedents, e.g. the polymeric species  $\text{As}_2\text{Te}_5^{2-}$ ,<sup>4</sup>  $\text{KSnTe}_5$  or  $\text{RbSnTe}_5$ <sup>5</sup> and  $\{[\text{Ga}(\text{en})_3]_2(\text{Ge}_2\text{Te}_{15})\}_n$ <sup>6</sup> which are considered to incorporate cross-chaped  $\text{Te}_5^{6-}$  units.<sup>4,6</sup> A closer analogy to **4** is the bicyclic octatelluride dianion in  $[\text{K}(15\text{-crown-5})_2]_2\text{Te}_8$ .<sup>7</sup> Similarly to **4**, the  $\text{Te}_8^{2-}$  dianion is comprised of a  $\text{Te}^{2+}$  centre that chelates to two dianions,  $\text{Te}_3^{2-}$  and  $\text{Te}_4^{2-}$ , to form a spirocyclic system.<sup>7</sup>

The Te–Te bond distances of 3.014(2)–3.027(2) Å in **4** are comparable to the mean value of ca. 3.03 Å found for the spirocyclic  $\text{Te}_8^{2-}$  dianion,<sup>7</sup> but significantly shorter than the corresponding bonds in the cyclic tritelluride **3** (2.716(1) Å).<sup>2</sup> This elongation is presumably a result of the stronger lp–bp repulsions in the *pseudo*-octahedral  $\text{Te}_5$  unit of **4** compared to those in the *pseudo*-tetrahedral arrangement of the  $\text{Te}_3$  moiety in **3**. The geometry at  $\text{Te}_5$  in **4** is severely distorted from square-planar with mean bond angles of 75.16(4)° and 104.74(5)°. The latter value is remarkably close to that found for  $\langle \text{Te}-\text{Te}-\text{Te} \rangle$  (104.50(1)°) in **3**.<sup>2</sup>

The P–Te distances in **4** (range 2.438(4)–2.445(4) Å) are significantly shorter than those observed for the neutral tritelluride (**3**) (2.532(1)–2.540(1) Å) [ $^1J(\text{P}, \text{Te}) = 1029 \text{ Hz}$ ]<sup>2</sup> and slightly longer than those in the dianion **2** ( $d(\text{P}-\text{Te}) = 2.418(2)$ – $2.422(2)$  Å;  $^1J(\text{P}, \text{Te}) = 1590 \text{ Hz}$ ).<sup>2</sup> The  $^{31}\text{P}$  NMR spectrum of the reaction mixture of  $\text{I}_2$  oxidation of  $[\text{Na}(\text{TMEDA})]_2\mathbf{1}$  in toluene (Scheme 1) showed a major resonance at  $-73.7 \text{ ppm}$  [ $^1J(\text{P}, \text{Te}) = 1198 \text{ Hz}$ ], which is tentatively attributed to **4** on the basis of the correlation between  $d(\text{P}-\text{Te})$  and  $^1J(\text{P}, \text{Te})$  for this class of compounds.<sup>8</sup>

Interestingly, the Rh(III) complex  $\{\text{Cp}^*\text{Rh}[\{^t\text{BuN}(\text{Te})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{Te})\text{N}^t\text{Bu}\}_2\mu\text{-Te}\} (\mathbf{5})$ , which contains the same spirocyclic dianion as found in **4**, was obtained as a dark reddish black solid from the attempted metathesis of  $[\text{Li}(\text{TMEDA})]_2\mathbf{1}$  with one-half of a molar equivalent of the dimer  $[\text{Cp}^*\text{RhCl}_2]_2$  (Scheme 2).

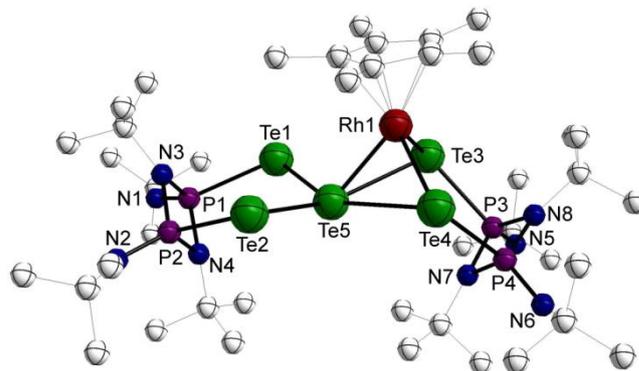


**Scheme 2** Formation of the Rh(III) complex **5**

The composition of **5** was established by the observation of the molecular ion with the appropriate isotopic composition in the electrospray mass spectrum. Recrystallisation from *n*-

hexane at  $-40 \text{ }^\circ\text{C}$  afforded crystals of **5** in the form of red needles, which were suitable for X-ray crystallography.<sup>9</sup> The molecular structure of **5** is depicted in Fig. 2 together with selected geometrical parameters involving the central  $\text{Te}_5$  unit.

Complex **5** incorporates the same dianion as was found in **4** but, in the case of the Rh(III) derivative, the spirocyclic ligand is coordinated through three tellurium centres to the rhodium atom to give an 18-electron complex. Expectedly, this coordination mode results in rather unequal Te–Te bond lengths in **6**. The  $\text{Te}_5$ – $\text{Te}_{1,2}$  bond distances of 2.817(1)–2.824(1) Å in the uncoordinated part of the  $\text{Te}_5$  unit in **2** are ca. 0.46 Å shorter than the mean distances involving the three-coordinate tellurium atoms ( $\text{Te}_3$  and  $\text{Te}_4$ ); they are also significantly shorter by ca. 0.20 Å than those in **4** (*vide supra*).



**Fig. 2** Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–Te5 2.8167(9), Te1–P1 2.502(2), Te2–Te5 2.8238(10), Te2–P2 2.502(2), Te3–Te5 3.2322(9), Te3–Rh1 2.6810(10), Te3–P3 2.503(2), Te4–Rh1 2.6590(9), Te4–P4 2.497(2), Te4–Te5 3.3268(9), Te5–Rh1 2.5476(9); Te5–Te1–P1 99.04(6), Te5–Te2–P2 98.74(5), Te5–Te3–Rh1 49.98(2), Te5–Te3–P3 100.64(6), Rh1–Te3–P3 108.77(5), Rh1–Te4–P4 108.39(6), Te1–Te5–Te2 104.85(2), Te1–Te5–Te3 81.31(2), Te1–Te5–Rh1 104.22(3), Te2–Te5–Te3 159.46(3), Te2–Te5–Rh1 105.84(3), Te3–Te5–Rh1 53.70(2), Te3–Rh1–Te4 102.47(3), Te3–Rh1–Te5 76.32(3),

The Rh atom in **5** is coordinated in a pyramidal  $\text{Te}, \text{Te}', \text{Te}''$ -mode to the  $\text{Te}_5$  unit. The Rh–Te distances of 2.681(1) and 2.659(1) Å to the three-coordinate Te centres,  $\text{Te}_3$  and  $\text{Te}_4$ , respectively, are significantly longer than the value of 2.548(1) Å for the five-coordinate  $\text{Te}_5$  atom, presumably because the latter is formally a  $\text{Te}_2^{2+}$  centre. Although Rh coordination to three tellurium centres is rare, it has been reported before, e.g. in the rhodium (II) complex  $[\text{RhCp}^*(\text{Te}(\text{CH}_2\text{CH}_2\text{CH}_2\text{TePh}_2))] [\text{PF}_6]^{10}$  in which the Rh–Te bond distances are in the narrow range 2.602(1)–2.618(1) Å and the Rh(I) complex  $[\text{Rh}(\text{COD})\{\text{Me}(\text{CH}_2\text{TeMe}_3)\}]^+$  with Rh–Te bond lengths of 2.692(1), 2.623(1) and 2.579(1) Å, which mirror those observed in **5** quite closely.<sup>11</sup> In contrast to the variation in the Te–Te bond distances in **5**, the P–Te bond lengths are in the narrow range 2.497(2)–2.503(2) Å, despite the different coordination numbers of the  $\text{Te}_{1,2}$  and  $\text{Te}_{3,4}$  pairs of Te atoms.

As expected from the solid-state structure, the  $^{31}\text{P}$  NMR spectrum of **5** exhibits two resonances: (a) a singlet at  $-123.4$  ppm accompanied by  $^{125}\text{Te}$  satellites [ $^1J(\text{P},\text{Te}) = 1136$  Hz], which is attributed to the P1,2 pair of atoms, and (b) a doublet due to coupling to  $^{103}\text{Rh}$ ,  $I=1/2$ , 100% at  $-126.8$  ppm [ $^2J(\text{P},\text{Rh}) = 4.5$  Hz and  $^1J(\text{P},\text{Te}) = 1270$  Hz] assigned to P3,4. No evidence for fluxional behaviour, e.g. exchange of the Rh atom between the P3,4 and P1,2 sites, was obtained from the NMR studies at room temperature.

In summary, we have reported the unexpected formation of a spirocyclic  $\text{Te}_5$  dianion anchored by  $\text{P}_2\text{N}_2$  rings. The multiple hard (N) and soft (Te) donor centres in this unusual ligand portend a versatile coordination chemistry as manifested by the structural determinations of the disodium and, especially,  $\text{Cp}^*\text{Rh}(\text{III})$  complexes. Further studies of main-group and transition-metal complexes are warranted. To this end the direct synthesis of **4** from the reaction of  $[\text{Na}(\text{TMEDA})]_2\mathbf{1}$  with the cyclic tritelluride **3** will be pursued (*vide supra*).

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## Notes and references

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Electronic supplementary information available: Experimental and crystallographic data in pdf format. CCDC 1029247 and 1029429 for **4** and **5**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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## COMMUNICATION

**TOC entry**

The versatile coordinating ability of a novel spirocyclic,  $P_2N_2$ -supported  $Te_5$  dianion is exemplified by N,N'-bonding to  $Na^+$  ions and Te,Te',Te'' linkages to a  $Cp^*Rh(III)$  group.

