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New tellurium-containing ring systems[1]

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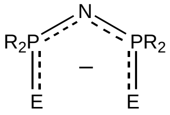
Abstract

The recent discovery of a suitable synthesis of the monoanionic ditelluroimidodiphosphinate ligands $[TePR_2NPR_2Te]^-$ (R = Ph, ^{i}Pr, ^{t}Bu) has facilitated investigations of the fundamental chemistry of these chelating inorganic ligands. This article is focused on aspects of that chemistry in which the behaviour of this ditelluro PNP ligand differs from that of the well-studied dithio and diseleno congeners. The emphasis is on new tellurium-containing ring systems formed in (a) redox transformations and (b) the synthesis of metal complexes.

1. Introduction

Dichalcogenoimidodiphosphinate anions $[EPR_2NPR_2E]^-$ (**1**) are acyclic ligands[2] in which two chalcogens are bridged by a PNP fragment that has two aryl or alkyl substituents on each P atom. The coordination chemistry of the dioxo, dithio and diseleno PNP monoanionic ligands has been studied in great detail [1-3]. A number of uses or potential uses for metallocyclic complexes of **1** have been identified, *e.g.* as lanthanide shift reagents, in luminescent materials, or in metal-extraction processes. More recently, O'Brien and co-workers have demonstrated in an extensive series of papers that metal complexes of the *iso*-propyl-substituted ligand $[SeP^iPr_2NP^iPr_2Se]^-$ are suitable single-source molecular precursors for the formation of thin films of semi-conducting metal selenides, *e.g.* MSe (M = Zn, Cd) [4], HgSe [5], and Bi_2Se_3 [6], by using the technique of aerosol-assisted chemical vapour deposition (AACVD). The cadmium complex can also be used to generate CdSe quantum dots via a solvothermal process [7].



1 (R = Ph, E = O, S, Se, Te)

Ditelluro PNP ligands (**1**, E = Te) were not reported until 2002 [8]. This short personal account reviews the developments that have occurred over the last five years from investigations of the fundamental chemistry of this new member of a well-studied class of inorganic ligands. The emphasis is on new tellurium-containing ring systems formed in (a) redox transformations and (b) the synthesis of metal complexes of **1** (E = Te, R = Ph, ^{i}Pr, ^{t}Bu).

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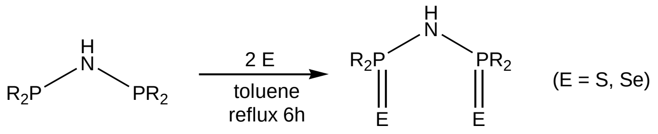
[2] For simplicity, *dichalcogenoimidodiphosphinates* will be referred to as *dichalcogeno PNP* ligands in this article

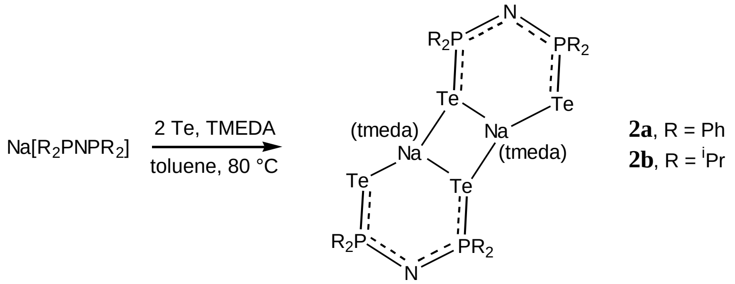
2. Synthesis of dichalcogenoimidodiphosphinate ligands

The anionic ligands are prepared by deprotonation of the NH group in the neutral precursors EPR$_2$N(H)PR$_2$E which, in the case of E = S, Se, are readily obtained by oxidation of the corresponding phosphorus(III) system with sulfur or selenium in boiling toluene (Eq. 1) [9, 10].



(1)

This approach is not effective for the synthesis of ditelluro PNP ligands because the direct reaction of the phenyl-substituted derivative PPh$_2$N(H)PPh$_2$ with tellurium does not result in significant oxidation even after prolonged periods in boiling toluene [8]. Consequently, we decided to prepare the anion [PPh$_2$NPPh$_2$]$^-$, as the sodium salt, by using a literature procedure [11] in the expectation that the negative charge would enhance the nucleophilicity of the phosphorus centres and thus facilitate the oxidation by tellurium. Indeed, the subsequent reaction of the PNP anion with tellurium in hot toluene containing TMEDA produces the ditelluro PNP ligand as the sodium salt **2a** in 50-60% yields (Eq. 2) [8]. This procedure can also be used for the synthesis of the *iso*-propyl-substituted derivative **2b** in >80% yields [12].



(2)

3. Structures of sodium salts of [TePR$_2$NPR$_2$Te]$^-$ anions

The sodium salt {[Na(TMEDA)][TePPh$_2$NPPh$_2$Te]}$_2$ (**2a**) is a centrosymmetric dimer in which the ligand is chelated through the two tellurium atoms to a sodium centre. In the solid state the P-Te bond lengths are slightly different (by 0.06 Å) because of the difference in the coordination number of the two tellurium centres. In solution, however, only one resonance is observed in both the ^{31}P and ^{125}Te NMR spectra at 235 K, suggesting either a rapid exchange process, even at low temperature, or dissociation of the dimer into two monomers via solvation of the sodium centres by the THF solvent [8].

In the absence of chelation of the sodium ions by TMEDA, the sodium salt of the *iso*-propyl-substituted PNP ligand $\{Na[TeP^iPr_2NP^iPr_2Te]\}_\infty$ (**3**) assumes a polymeric structure in which the chair-shaped dimeric units are linked through Na---Te interactions to give a motif in which Na_2Te_2 rings are conjoined through two spiro sodium ions (Fig. 1) [13] These four-membered rings form rhombohedra with Na-Te distances in the range 3.13 – 3.19 Å and endocyclic bond angles of 86.0 ° and 94.0 ° (for rings involving Te2) and 81.8 ° and 98.2 ° (for rings involving Te1). The P-Te bond distances in **3** are equal within experimental error, since both tellurium centres are three-coordinate in this structure. A similar extended-ladder structure has been reported for the sulfur-containing system $\{K[SPPh_2NPPh_2S]\}_\infty$ [14].

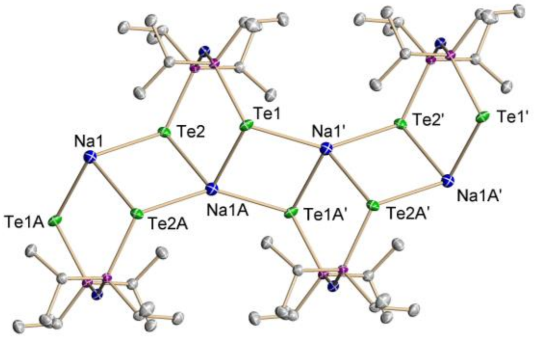
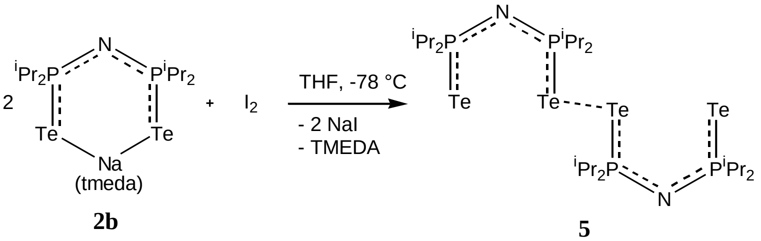


Figure 1

4. Redox transformations of $[EPR_2NPR_2E]^-$ (E = S, Se, Te) anions

a. Dimer formation

The *iso*-propyl derivative $P^iPr_2N(H)P^iPr_2$ is more reactive than the phenyl-substituted analogue towards tellurium, and the monotelluride $P^iPr_2(H)NP^iPr_2Te$ (**4**) is obtained as the P-H tautomer in 81% yield at room temperature in hexane [8]. Upon exposure to air, a pale yellow hexane solution of the monotelluride **4** becomes dark red. An X-ray structure determination of the red crystals obtained from such a solution revealed the product to be the centrosymmetric dimer ($TeP^iPr_2NP^iPr_2Te$-)$_2$ (**5**) in which the central Te-Te bond is about 0.20 Å longer than a typical Te-Te distance as seen in organic ditellurides (Fig. 2) [8]. The formation of the ditelluride **5** by this route is inconveniently slow. From the structure determination, however, it was evident that **5** is a dimer of the neutral radical ($TeP^iPr_2NP^iPr_2Te$)$^\bullet$. Consequently, we developed an improved synthesis that involves the one-electron oxidation of the corresponding anion with stoichiometric amounts of iodine to give **5** in 87% yield (Eq. 3).



2b **5** (3)

Since this type of redox behaviour has not been reported for the well-studied dithio or diseleno PNP ligands [1-3], we decided to carry out a systematic investigation of the one-electron oxidation of these monoanionic ligands as function of (a) the chalcogen and (b) the alkyl substituent on the two phosphorus atoms.

The initial experiments showed that the reaction of the sulfur derivative Na[$SP^iPr_2NP^iPr_2S$] with half-an-equivalent of I_2 in THF or benzene yields a mixture of three phosphorus-containing products one of which has been identified $SP^iPr_2N(H)P^iPr_2S$ [15]. By contrast, the oxidation of sodium salt of the *tert*-butyl substituted derivative Na[$SP^tBu_2NP^tBu_2S$] with half-an-equivalent of iodine produced the disulfide ($SP^tBu_2NP^tBu_2S$-)$_2$ (**6**) in 68% yield (Fig.2). Similar one-electron oxidations of the selenium-containing salts Na[$SePR_2NPR_2Se$] (R = ^{i}Pr, ^{t}Bu) produce the corresponding diselenides ($SePR_2NPR_2Se$-)$_2$ (**7**, R = ^{i}Pr; **8**, R = ^{t}Bu) in *ca.* 90% yields (Fig. 2) [15]. Although the conformations of **7** and **8** differ significantly, the common feature of all these dichalcogenides is a central E-E bond that is elongated compared to the corresponding chalcogen-chalcogen single-bond lengths [by *ca.* 8% (E = Te), 6% (E = Se) or 2% (E = S)].

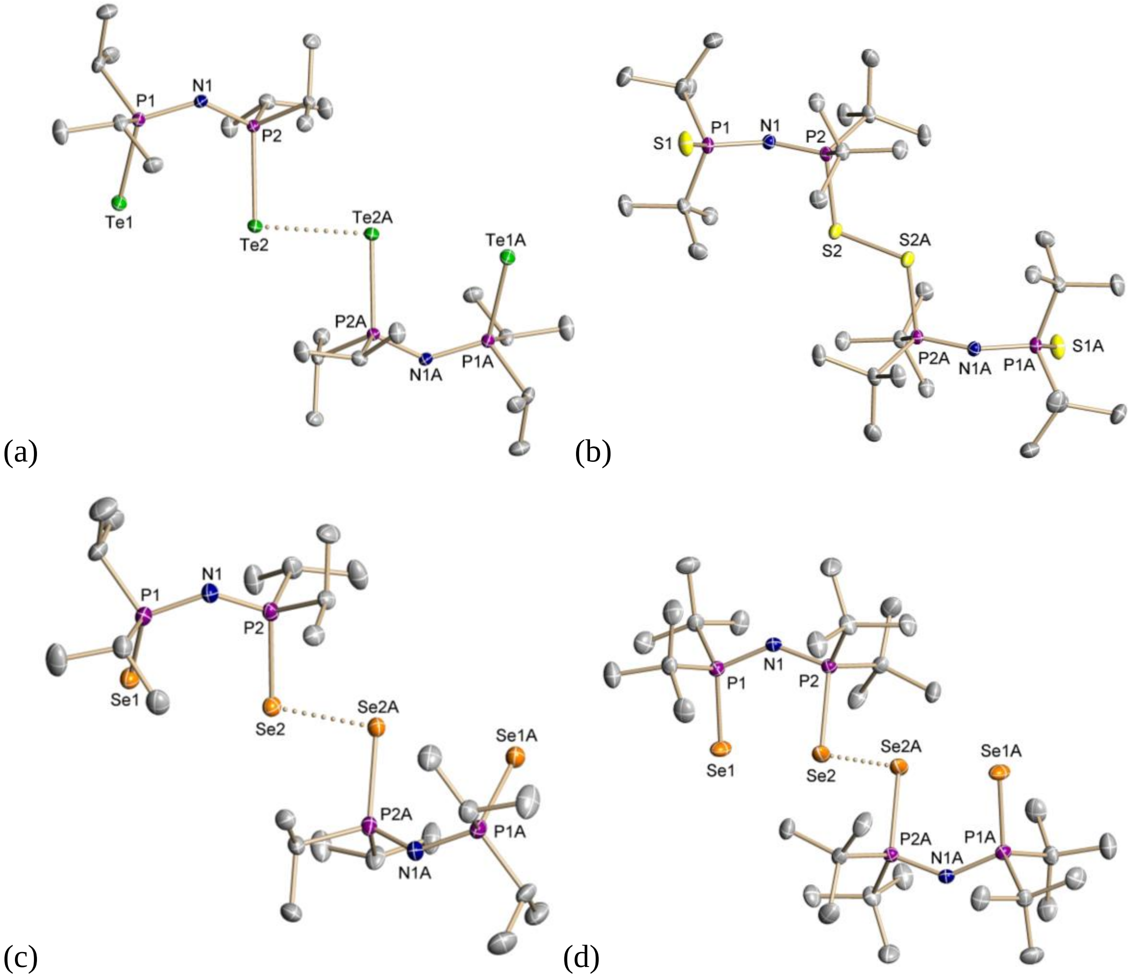


Figure 2

In order to complete this study on the one-electron oxidation of $[EPR_2NPR_2E]^-$ anions, we investigated the influence of *tert*-butyl substituents for the tellurium system. The incentive for this was the prediction from DFT calculations that the Te-Te bond length in the *tert*-butyl derivative would be significantly longer than that in the *iso*-propyl analogue **5**, raising the possibility of dissociation into monomeric radicals $(Te^tBu_2PNP^tBu_2Te)^{\bullet}$ in solution [8].

The synthesis of the dimer $(Te^tBu_2PNP^tBu_2Te\text{-})_2$ (**9**) was carried out in the same manner as that of the *iso*-propyl analogue. However, an X-ray structural determination revealed a different conformation than that observed for the *iso*-propyl analogue **5** [15]. As illustrated in Fig. 3, three of the tellurium atoms in **9** are aligned in an almost linear fashion with Te-Te distances of 2.98 and 3.10 Å. This structural arrangement is comparable with that observed for the acyclic species $[Te_3Ph_3]^-$ [16] and $[Te_3Ph_3]^+$ [17], which both exhibit elongated Te-Te bonds. The third Te-Te distance is 3.25 Å. These structural data suggest the occurrence of an internal redox process that gives rise to a contact-ion pair, which can be viewed as a spirocycle formed by asymmetric chelation of the acyclic ditelluro PNP anion to one tellurium atom of a cyclic $[(TeP^tBu_2)_2N]^+$ cation (Fig. 3).

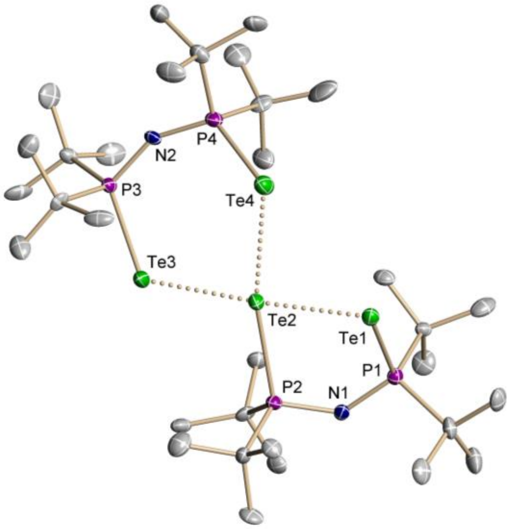
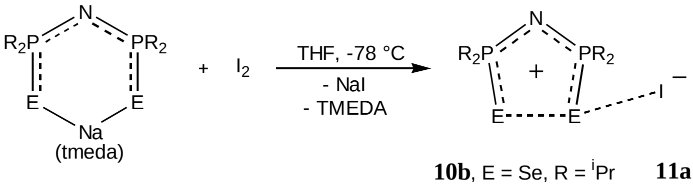


Figure 3

This structural description of **9** suggested that an alternative synthetic approach to these dimeric systems involving reaction of an acyclic dichalcogeno PNP anion with the corresponding $[(EPR_2)_2N]^+$ cation might lead to the formation and isolation of other examples of contact-ion pairs. In addition, these anion-cation reactions afford the intriguing possibility of generating dimeric, mixed chalcogen systems. Thus, the next challenge was to prepare the cyclic cationic systems.

b. Formation of cyclic cations, $[(EPR_2)_2N]^+$ (E = S, Se, Te) and $[Se(SePR_2)_2N]^+$

The obvious route to dichalcogeno PNP cations is the *two-electron* oxidation of the corresponding anions. Indeed, the reactions of the sodium salts of diseleno and ditelluro PNP anions with one equivalent of iodine in THF produce the corresponding cations as the iodide salts **10b** and **10c** in excellent yields (Eq. 4) [18]. These salts are dark red powders, which are remarkably air stable for periods of several months. They are the first examples of the cyclic $[(EPR_2)_2N]^+$ cations (E = Se, Te). The sulfur-containing ring system $[(SPR_2)_2N]^+$ is not obtained as the iodide salt **10a** when the substituents attached to phosphorus are *iso*-propyl. However, the *tert*-butyl substituted cation $[(SP^tBu_2)_2N]^+$ is obtained in high yield as the triiodide salt **11a** by oxidation of the corresponding anion with two equivalents of iodine [15].



(4)

10b, E = Se, R = ^{i}Pr **11a**, E = S, R = ^{t}Bu (anion = I_3^-)

10c, E = Te, R = ^{i}Pr **11b**, E = Se, R = ^{t}Bu

13c, E = Te, R = Ph **11c**, E = Te, R = ^{t}Bu

Simple electron-counting procedures [19] predict that five-membered rings of the type $[(EPR_2)_2N]^+$ (E = S, Se, Te) are formally six π-electron systems. DFT calculations have provided important insights into the electronic structures of these cations. As illustrated in Fig. 5, the three highest occupied molecular orbitals are indeed π-type orbitals. The π-bond order is low, however, since the bonding effect of the E-E π-bonding orbital (HOMO-2) is approximately cancelled by the double occupation of the E-E π*-antibonding orbital (HOMO) and the third occupied π-orbital is a primarily non-bonding nitrogen-centered orbital (HOMO-1).

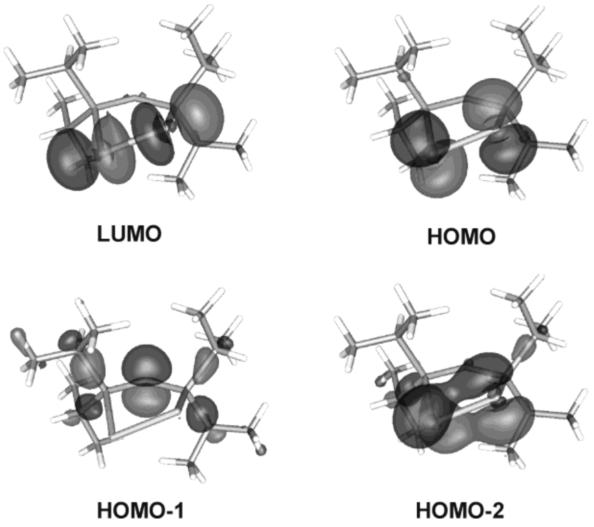


Figure 5

The structures of the iodide salts **10b** and **10c** have been characterized in the solid state by X-ray diffraction and shown to consist of five-membered rings that are distinctly non-planar [18]. The cationic rings are linked by I^- ions to give an infinite chain (Fig. 6). Significantly, the chalcogen-chalcogen bond lengths in these rings are about 6-7 % longer than typical single-bond values. This elongation is attributed to donation of electron density from a lone pair on the iodide counterion into the σ* (E-E) orbital (LUMO) of the ring system. Support for this proposed electron-transfer process comes from the preparation of the salts $[(EP^iPr_2)_2N][SbF_6]$ (**12b**, E = Se, **12c**, E = Te) by treatment of **10b** or **10c** with $Ag[SbF_6]$ in toluene [20]. The anion-cation interactions in **12b** and **12c** are extremely weak and the E-E bond lengths are typical single bonds (Table 1).

The synthetic approach used in Eq. 4 can also be applied to the preparation of the phenyl-substituted derivative $[(TePPh_2)_2N]I$ (**13c**) [20]. In contrast to the *iso*-propyl analogue **10c**, the iodide salt **13c** adopts a dimeric structure in the solid state (Fig. 6). Dimeric structures are also observed for the *tert*-butyl derivatives $[(EP^tBu)_2N]I$ (**11b**, E = Se; **11c**, E = Te) [15], prepared in a similar manner (Eq. 4) and the chloride salt $[(TeP^iPr_2)_2N]Cl$ (**14**), which is obtained in low yield from the reaction of $Na[(TeP^iPr_2)_2N]$ with sulfuryl chloride [20] (Fig. 6).

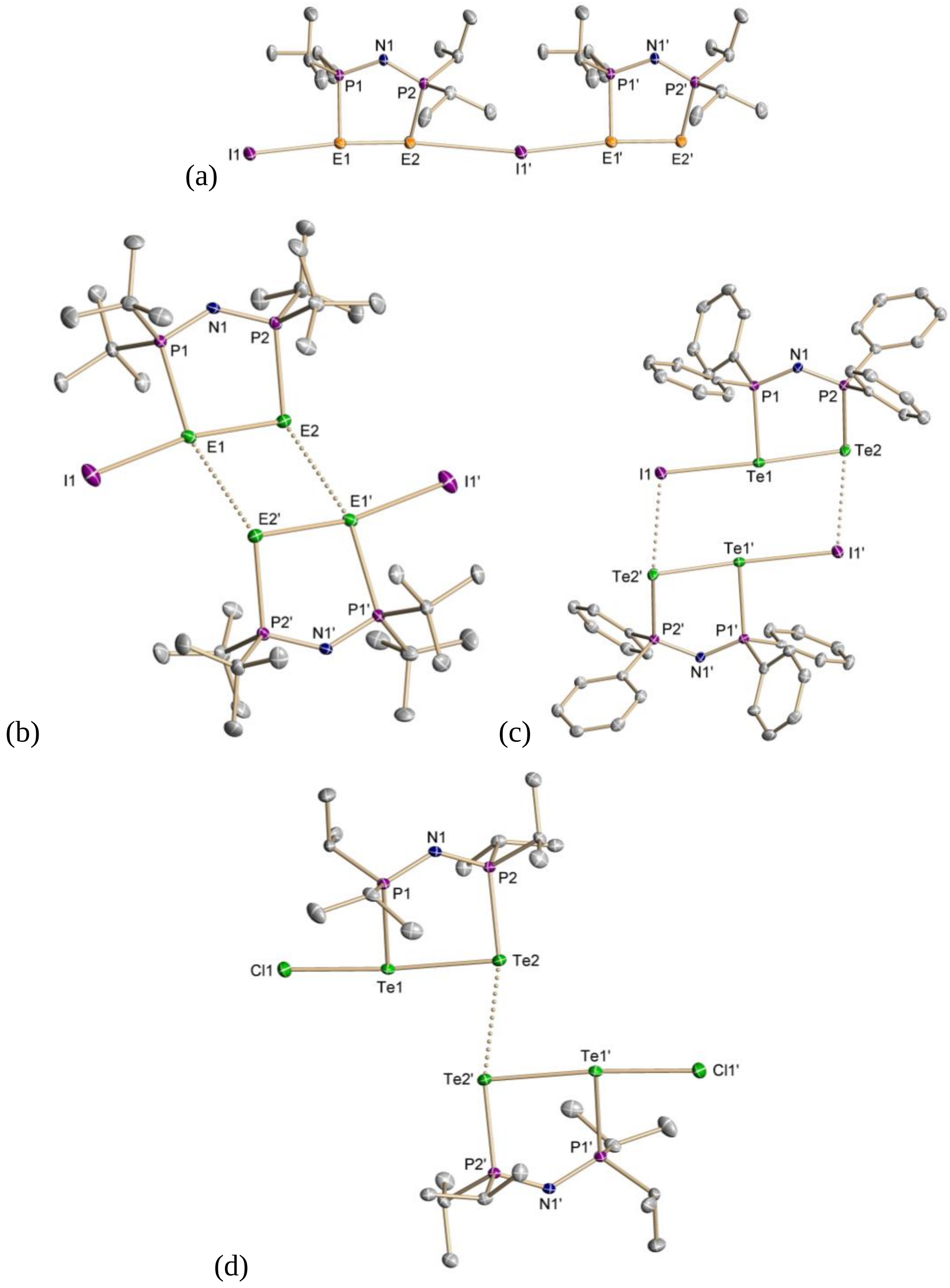
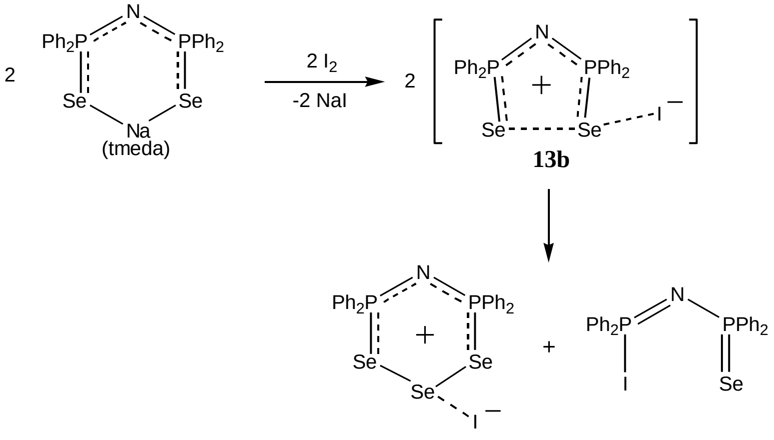

N1
P1
P2
N1'
P1'
P2'
I1
E1
E2
I1'
E1'
E2'
(a)
N1
P1
P2
E1
E2
I1
I1'
E2'
E1'
P2'
N1'
P1'
(b)
N1
P1
P2
Te2
I1
Te1
Te1'
I1'
Te2'
P2'
P1'
N1'
(c)
N1
P1
P2
Cl1
Te1
Te2
Te1'
Cl1'
Te2'
P1'
P2'
N1'
(d)

Figure 6

A change of substituents on phosphorus from *iso*-propyl to phenyl has an unanticipated influence on the outcome of the two-electron oxidation in the case of the diseleno PNP anion. The five-membered selenium-containing cation $[(SePPh_2)_2N]^+$ is not isolated upon reaction of $Na[SePPh_2NPPh_2Se]$ with iodine. Instead, decomposition to give the dimeric salt $\{[Se(SePPh_2)_2N]I\}_2$ (**15**), in which the cation is a six-membered ring in a chair conformation with three adjacent Se atoms, together with the acyclic compound $SePPh_2NPPh_2I$ (**16**) was observed (Scheme 1) [20]. A similar cationic six-membered ring in which the trichalcogeno fragment is STeS has previously been reported as the chloride salt [21].



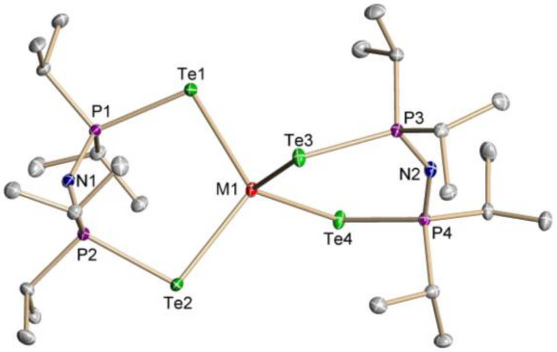
15 **16**

Scheme 1

The decomposition of the salts $[(EPR_2)_2N]I$ (E = Se, Te: R = ^iPr, Ph) into iodide salts of the corresponding six-membered ring $\{[E(EPR_2)_2N]I\}$ and the acyclic product (depicted in Scheme 1 for the hypothetical species **13b**) has been investigated through DFT calculations. The calculated thermochemical energies for this process are endothermic by 50-80 kJ mol^{-1} for all derivatives except **13b**, for which this transformation is predicted to be thermoneutral [20]. Thus the DFT calculations provide some support for the anomalous behaviour of $Na[SePPh_2NPPh_2Se]$ upon oxidation.

5. Metal complexes of $[TePR_2NPR_2Te]^-$ ligands

In view of the work of O'Brien *et al*. on the AACVD generation of metal selenide thin films [4-6], a primary incentive of the synthesis of metal complexes of $[TePR_2NPR_2Te]^-$ ligands is their potential use as single-source molecular precursors to metal tellurides. In this context, the *iso*-propyl derivative of this ligand is of more interest than the phenyl derivative because of the higher volatility of its metal complexes. The sodium salt $[Na(TMEDA)] [TeP^iPr_2NP^iPr_2Te]$ (**2b**) has been used to prepare a variety of homoleptic complexes by metathetical reactions with the appropriate metal halides. For example, the group 12 complexes, $M[(TeP^iPr_2)_2N]_2$ (**17a**, M = Zn; **17b**, M = Cd; **17c**, M = Hg) are obtained in 55-83% yields and have been shown to adopt the expected distorted tetrahedral structures in the solid state (Fig.7a) [12]. The cadmium complex **17b** has been found to be a suitable source of pure cubic CdTe thin films by using AACVD techniques in the temperature range 425-475 °C [22]. The group 15 complexes $M[(TeP^iPr_2)_2N]_3$ (**18a**, M = Sb; **18b,** M = Bi) have been prepared in *ca*. 85% yields and have been shown to have distorted octahedral structures in the solid state (Fig. 7b) [12]. The antimony complex **18a** produces pure rhombohedral Sb_2Te_3 nanoplates via AACVD at 375-475 °C [23].



(a)

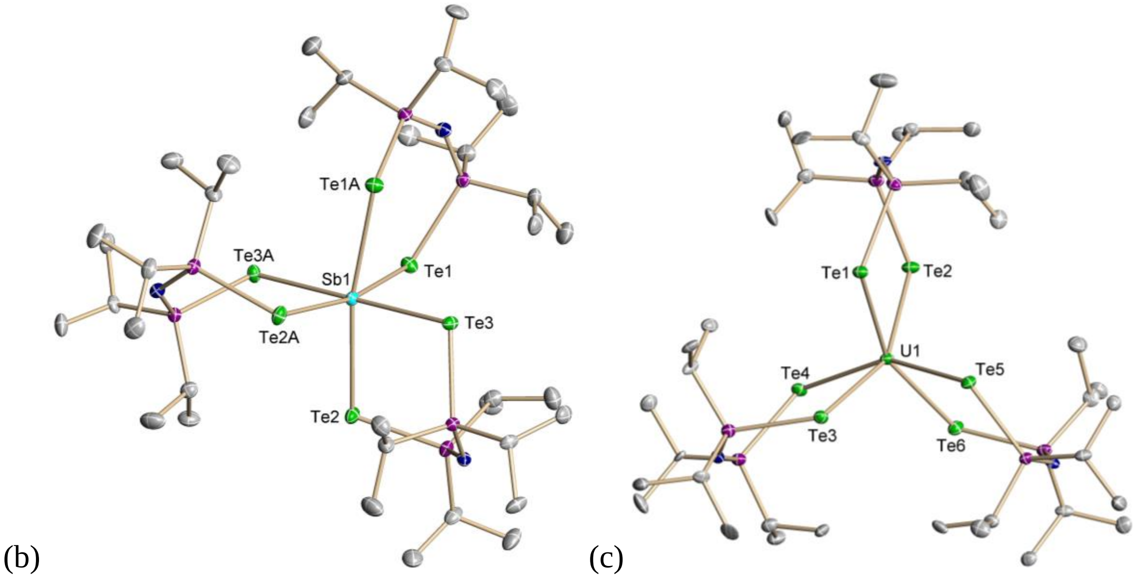


Figure 7

In solution, the covalent homoleptic complexes **17a-c**, **18a** and **18b** exhibit well-resolved ^{125}Te satellites in the ^{31}P NMR spectra with P-Te coupling constants in the narrow range 1280-1340 Hz, substantially smaller than the value of 1487 Hz observed for the corresponding Na^+ salt [12] in d_8-THF. Consistently, the P-Te bond lengths are significantly longer in these metal complexes.

Gaunt *et al*. have reported the synthesis of the homoleptic, six-coordinate lanthanum(III) and uranium(III) complexes $M[(TeP^iPr_2)_2N]_3$ (**19a**, M = La; **19b**, M = U) in 40-50% yields via metathetical reactions of **2b** with the corresponding metal triiodide [24]. Both **19a** and **19b** exhibit distorted trigonal–prismatic structures (Fig. 7c). The uranium(III) complex **19b** is the first example of a molecular compound containing an actinide-tellurium bond. The structural parameters for **19a** and **19b** suggest more covalent character in the U-Te bond than the La-Te bond [24].

Initial investigations of coinage metal complexes of $[TePR_2NPR_2Te]^-$ (R = ^{i}Pr, Ph) ligands have revealed some significant differences in their structures compared to those of the analogous complexes of dithio or diseleno PNP ligands. The strong reducing power of ditelluro PNP anions is clearly evident in the direct reaction of **2b** with AuCl. In THF, even at -78 °C, this reaction is extremely vigorous and results in the deposition of Au metal (an expensive way of making gold!). In the presence of triphenylphosphine, however, the monomeric complex **20** was isolated in good yield [25] (Fig. 8). The selenium analogue of **20** has been reported by Schmidbaur *et al*. [26]. The only significant difference in the structures of these two gold complexes is that the ditelluro PNP ligand is bonded symmetrically to the metal whereas the diseleno PNP ligand forms Au-Se bonds that differ in length by 0.11 Å.

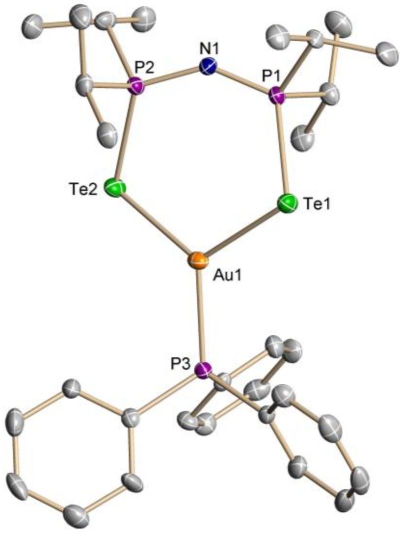


Figure 8

In contrast to the observations with AuCl, metathesis of silver(I) iodide with **2b** proceeds in a straightforward manner to give the homoleptic complex $\{Ag[(TeP^{i}Pr_2)_2N]\}_6$ (**21**) [25]; the corresponding selenium complex is trimeric [27]. The hexameric complex **21** exhibits an unprecedented twelve-membered ring structure (Fig. 9) in which the six silver centres are all in a three-coordinate trigonal planar environment (sum of bond angles 357-360°). Nevertheless, the Ag(2) and Ag(3A) centres are in close proximity with Ag-Ag distances of 2.95 Å, in the range for which a metallophilic d^{10}-d^{10} interaction should be considered [28]. However, this close approach may simply be a result of the conformational flexibility of the twelve-membered ring in **21** combined with the need to minimize interactions between *iso*-propyl groups.

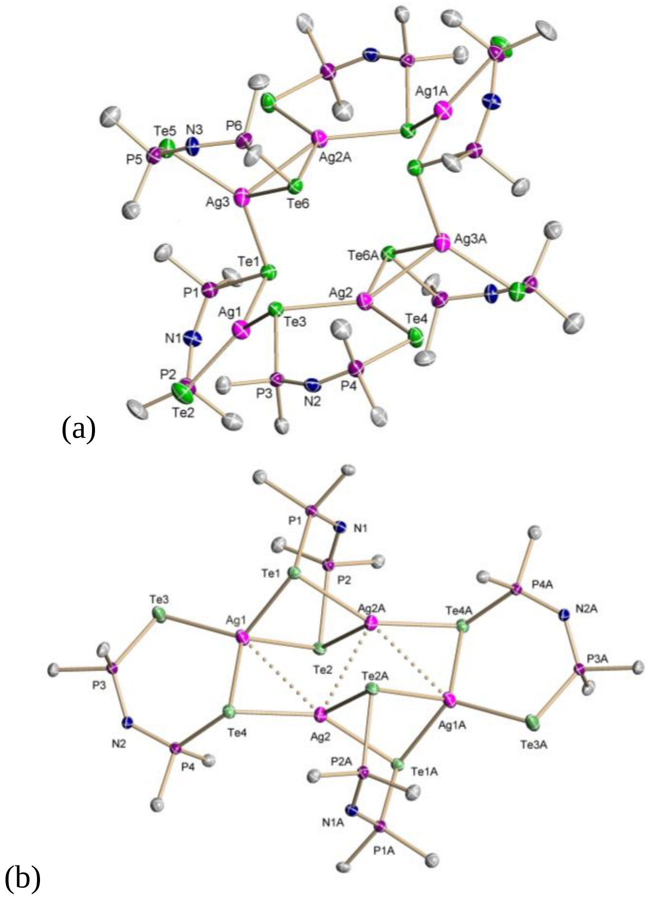


Figure 9

A change of the substituents on phosphorus from *iso*-propyl to phenyl has an interesting influence on the structure of the Ag(I) complex obtained. The reaction of **2a** with AgI generated a tetrameric complex $\{Ag[(TePPh_2)_2N]\}_4$ (**22**) with a chair-shaped eight-membered (Ag_4Te_4) ring (Fig. 9) [25]. There are two distinct silver environments in the centrosymmetric structure of **22**; Ag(1) is connected to four tellurium atoms in a distorted tetrahedral arrangement, whereas Ag(2) is bound to only three tellurium atoms and displays a trigonal geometry that is distorted towards pyramidal (sum of bond angles is 344.8^o). This distortion brings Ag(2) and its symmetrical equivalent Ag(2A) into relatively close contact, 2.992(2) Å suggesting that this relatively short Ag-Ag distance represents a metallophilic interaction. It is pertinent to note the ability of the ditelluro PNP ligand to act as a doubly bridging ligand in which both tellurium atoms bridge two metal centres in **22**. The other chelating ligand adopts a bonding mode in which one chalcogen is two-coordinate and the other is three-coordinate.

The reaction of **2b** with copper(I) chloride also proceeds in a straightforward manner to give a homoleptic copper(I) complex **23c** in 75% yield [25]. The X-ray structure of **23c** revealed that it is trimeric like the corresponding sulfur and selenium complexes, respectively (Fig. 10) [29, 27]. However, the tellurium derivative **23c** exhibits significant structural differences compared to **23a** and **23b**, in which all three ligands are coordinated to the copper centres via one two-coordinate and one three-coordinate chalcogen atom. The latter bridges two copper centres in **23a** and **23b** giving rise to a symmetrical, six-membered Cu_3E_3 ring. By contrast, only two of the ligands adopt this mode of coordination in **23c**, while the third acts as a doubly bridging ligand with two three-coordinate tellurium sites. Possibly as a consequence of this, two of the Cu-Cu distances are much shorter than the third (2.637(2) and 2.626(2) vs. 3.581(1) Å), suggesting the possibility of metallophilic (d^{10}-d^{10}) interactions between these metal centres.

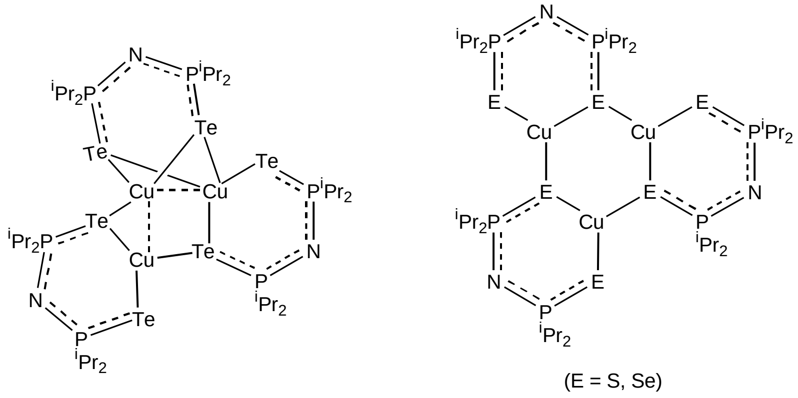


Figure 10

6. Tellurium-transfer reactions: formation of Ga_2Te_2 and M_3Te_3 (M = Ga, In) rings

In contrast to the formation of homoleptic complexes in metathetical reactions of **2b** with group 11, 12 and 15 halides and with lanthanide or uranium triiodides, the reaction of **2b** with group 13 trihalides resulted in an unprecedented tellurium-transfer reaction [30]. Our work on group 13 systems commenced with the reaction of Me_2AlCl with **2b**. The product was extremely air-sensitive and exhibited a P-Te coupling constant of 1560 Hz, significantly larger than the values of 1487 Hz for the Na^+ salt or 1280-1340 Hz for covalent derivatives of the $[TeP^iPr_2NP^iPr_2Te]^-$ ligand [12]. An X-ray structural determination revealed it to be the ion-separated salt $[Me_2Al(TMEDA)]$ $[TeP^iPr_2NP^iPr_2Te]$ (**24**) comprised of the acyclic $[TeP^iPr_2NP^iPr_2Te]^-$ anion and the TMEDA-solvated Me_2Al^+ cation (Fig.11) [31].

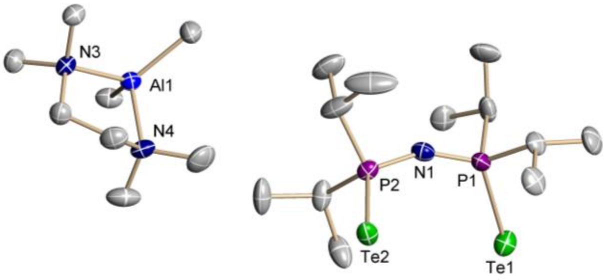
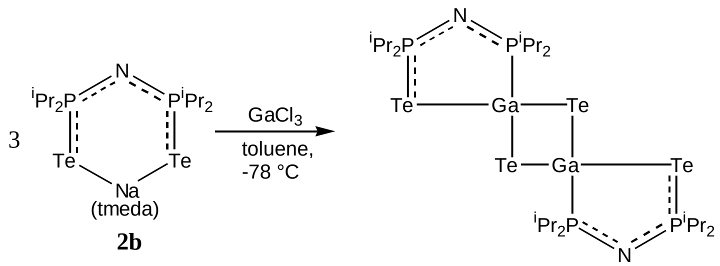


Figure 11

Attempts to make a homoleptic aluminum(III) complex by treatment of $AlCl_3$ with three equivalents of **2b** gave a complex mixture of products [31]. Consequently, we turned our attention to the heavier group 13 metals. Interestingly, an attempt to prepare a gallium(III) complex by treatment of gallium trichloride with one equivalent of **2b** produced the complex **25** that was shown by X-ray crystallography to contain a central four-membered Ga_2Te_2 ring [30]. Instead of a straightforward metathesis, the $[TeP^iPr_2NP^iPr_2Te]^-$ ligand has given up one tellurium atom in the formation of the Ga_2Te_2 ring; the remaining ligand is the monotelluride $[P^iPr_2NP^iPr_2Te]^-$, which is chelated to the metal by a P and a Te atom. (Eq. 5). The tellurium atoms of the two monotelluride ligands in the isolated complex **25** are in a *trans* arrangement with respect to the Ga_2Te_2 ring. However, the NMR spectrum of the reaction mixture shows two sets of mutually coupled doublets, suggesting that the *cis* isomer is also present in solution [30]. Previous examples of chalcogen transfer from a dichalcogeno PNP ligand to a metal centre include sulfur or selenium to ruthenium [32] and sulfur to antimony [33].

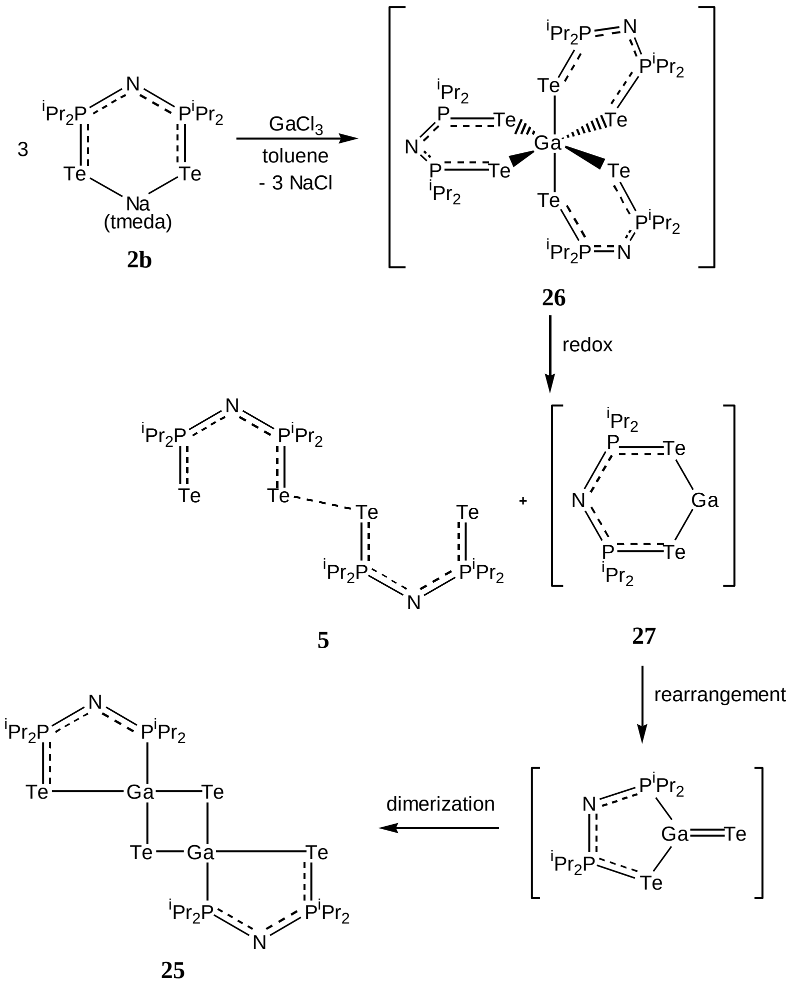


2b

25

(5)

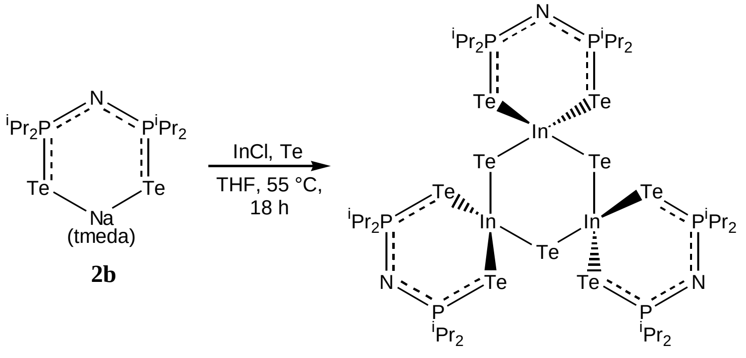
In an attempt to elucidate the pathway involved in the formation of the Ga_2Te_2 ring, the reaction of **2b** with $GaCl_3$ was carried out in a 3:1 molar ratio in order to generate the octahedral gallium(III) complex **26** (Scheme 2). This reaction produces the ditelluride dimer **5** in *ca*. 90% yield, presumably via reductive elimination from the initially formed **26** (Scheme 2) [30]. We propose that the cyclic gallium(I) complex **27** formed in this process undergoes a redox rearrangement to give the gallatellurone **28**, which, in the absence of kinetic stabilization by very bulky groups [34], will dimerize to give the four-membered ring **25**.



Scheme 2

The reaction of **2b** with indium trichloride in a 1:1 molar ratio provides another example of tellurium transfer, but the product is different than that obtained from gallium trichloride. The ^{31}P NMR spectrum of the reaction mixture revealed the formation of several products, one of which (**29**) was isolated and shown to consist of a central six-membered In_3Te_3 ring in a distorted boat conformation with each indium atom chelated by a $[TeP^iPr_2NP^iPr_2Te]^-$ ligand. Several different architectures, including cubes [35, 36] and four-membered rings [37, 38], are known for indium-tellurium systems, but the In_3Te_3 ring is a new structural motif.

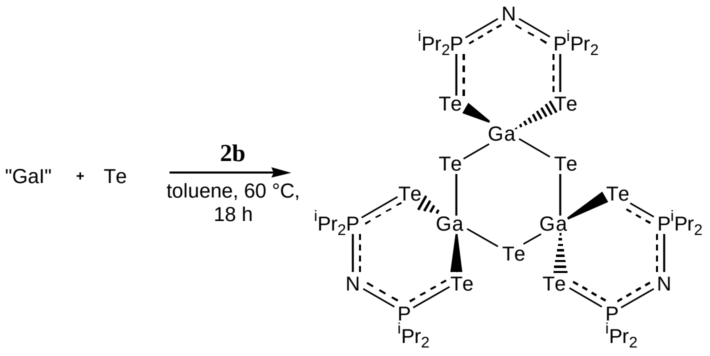
Although the ligands in **29** have retained both tellurium atoms, the transfer of tellurium to indium from sacrificial $[TeP^iPr_2NP^iPr_2Te]^-$ ligands has also occurred. Consequently, the yield of **29** is low. As an alternative synthesis, we decided to attempt the *in situ* generation of the In_3Te_3 ring from the reaction of indium(I) chloride with **2b** *in the presence of elemental tellurium* using one molar equivalent of each reagent. The complex **29** self-assembles under the reaction conditions depicted in Eq. 6 and can be isolated in 75% yield [30]. Complex **29** exhibits reasonable air and moisture stability and has been shown to serve as a suitable single–source precursor to thin films of cubic In_2Te_3 under AACVD conditions in the temperature range 375-475 °C [39].



2b **29**

(6)

This new methodology for the synthesis of group 13-tellurium rings can also be applied to gallium. The reaction of “GaI” [40] with **2b**, *in the presence of one equivalent of tellurium*, produces the analogous gallium complex **30** (Eq. 7) [30]. The ternary compounds GaSeBr and GaSBr, recently synthesized by Schmidbaur *et al.*, form soluble products with various pyridine ligands that contain Ga_3E_3 (E = S, Se) rings [41], but **30** is the first example of a six-membered Ga_3Te_3 ring. The gallium complex **30** is isostructural with **29**.



30

(7)

The attractive feature of this synthetic route to **29** and **30** is the formation of pure products in good yields. The methodology is potentially versatile, since it could be used to prepare mixed-chalcogen ring systems by using elemental sulfur or selenium instead of tellurium as the oxidant. Alternatively, the use of alkali-metal salts of the dithio or diseleno PNP ligand systems **1** (E = S, Se; R = ^{i}Pr) instead of **2b** may lead to mixed-chalcogen systems.

5. Conclusions

The discovery of the “metallation-first” approach to the synthesis of $[TePR_2NPR_2Te]^-$ ligands has paved the way for an investigation of the fundamental chemistry of this new member of the well-studied class of dichalcogeno PNP ligands. Studies of redox transformations involving these monoanionic ligands have revealed some new features of the chemistry of chalcogen compounds. One-electron oxidation by iodine produces dimers with two different structures depending on the substituents on the phosphorus atoms. In the case of the telluro species, one of these isomers can be described as a spirocyclic contact ion-pair while the other is an acyclic ditelluride with a long, central Te-Te bond. The sulfur and selenium systems form analogous acyclic dichalcogenides. Two-electron oxidation of the acyclic monoanionic ligands $[EPR_2NPR_2E]^-$ by iodine produces the first examples of the five-membered cyclic cations $[(EPR_2)_2N]^+$ (E = S, Se, Te). Although these new, electron-rich inorganic ring systems are formally six π-electron ring systems, DFT calculations show that the π-bond order is low.

The $[TePR_2NPR_2Te]^-$ ligands form homoleptic complexes with group 11, 12 and 15 metals as well as with lanthanum(III) and uranium(III). The structures of the silver and copper complexes are different from those of the corresponding dithio or diseleno PNP ligands. The preliminary results indicate that these differences result from the greater flexibilty of the ditelluro PNP ligands resulting from the larger atomic size of tellurium. This flexibility leads to a (a) larger ring sizes and (b) close metal-metal contacts suggestive of metallophilic (d^{10}-d^{10}) interactions [42]. A fascinating feature of the metal complex chemistry of $[TeP^{i}Pr_2NP^{i}Pr_2Te]^-$ ligands is the occurrence of tellurium transfer for the heavier Group 13 metals. The identification of the products of this chalcogen-transfer process led to the development of a new methodology for the synthesis of M-Te (M = Ga, In) ring systems stabilized by chelation of the $[TeP^{i}Pr_{2}NP^{i}Pr_{2}Te]^{-}$ ligand to the metal centres.

Details of the applications of the homoleptic metal complexes described in this paper for the generation of metal telluride thin films by AACVD techniques are discussed in the article by O'Brien *et al.* in this issue [43].

Acknowledgements

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References

[1] (a) A. Schmidpeter, R. Bohm, H. Groeger, Angew. Chem. Int. Ed. 3 (1964) 704; (b) A. Schmidpeter, K. Stoll Angew. Chem. Int. Ed. 6 (1967) 252. (c) A. Schmidpeter, K. Stoll, Angew. Chem., Int. Ed. 7 (1968) 549.

[2] For reviews of early work, see (a) C. Silvestru, J. E. Drake, Coord. Chem. Rev. 223 (2001) 117; (b) T. Q. Ly, J. D. Woollins, Coord. Chem. Rev. 176 (1998) 451; (c) I. Haiduc. in Comprehensive Coordination Chemistry II, J. A. McCleverty, T. J. Meyer (Eds.), Elsevier Ltd; Amsterdam (2003) 323-347.

[3] (a) H. Rudler, B. Denise, J. R. Gregorio, J. Vaissermann, Chem. Commun. (1997) 229; (b) S. W. Magennis, S. Parsons, A. Corval, J. D. Woollins, Z. Pikramenou, Chem. Commun. (1999) 61; (c) J. G. H. du Preez, K. U. Knabl, L. Krüger, B. J. van Brecht, Solvent Extr. Ion Exch. 10 (1992) 729.

[4] (a) M. Afzall, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien, J.-H. Park, J. D. Woollins, Eur. J. Inorg. Chem. (2004) 171; (b) M. Afzall, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien, J.-H. Park, J. Mat. Chem. 13 (2003) 639.

[5] D. J. Crouch, P. M. Hatton, M. Helliwell, P. O'Brien, J. Raftery, Dalton Trans. (2003) 2761.

[6] (a) J. Waters, D. Crouch, J. Raftery, P. O'Brien Chem. Mater. 16 (2004) 3289; (b) D. J. Crouch, M. Helliwell, P. O'Brien, J.-H. Park, J. Waters, Dalton Trans (2003) 1500.

[7] D. J. Crouch, P. O’Brien, M. A. Malik, P. J. Skabara, S. P. Wright, Chem. Commun. (2003) 1454.

[8] (a) G. G. Briand, T. Chivers, M. Parvez, Angew. Chem. Int. Ed. 41 (2002) 3468; (b) T. Chivers, D. J. Eisler, J. S. Ritch, H. M. Tuononen, Angew. Chem. Int. Ed. 44 (2005) 4953.

[9] D. Cupertino, D. J. Birdsall, A. M. Z. Slawin, J. D. Woollins, Inorg. Chim. Acta 290 (1999) 1.

[10] P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, J. Chem. Soc., Dalton Trans (1995) 1607.

[11] J. Ellermann, M. Schutz, F. W. Heinemann, M. Moll, Z. Anorg. Allg. Chem. 624 (1998) 257.

[12] T. Chivers, D. J. Eisler, J. S. Ritch, Dalton Trans. (2005) 2675.

[13] T. Chivers, D. J. Eisler, J. S. Ritch, Unpublished results.

[14] A. M. Z. Slawin, J. Ward, D. J. Williams, J. D. Woollins, J. Chem. Soc. Chem. Commun. (1994) 421.

[15] T. Chivers, D. J. Eisler, J. S. Ritch, H. M. Tuononen, Chem. Eur. J. to be submitted.

[16] J. Jeske, W. du Mont, P. G. Jones, Angew. Chem. Int. Ed. 36 (1997) 2219.

[17] A. C. Hillier, S.-Y. Liu, A. Sella, M. R. J. Elsegood, Angew. Chem Int. Ed. 38 (1999) 2745.

[18] J. Konu, T. Chivers, H. M. Tuononen, Chem. Commun. (2006) 1634.

[19] T. Chivers, A Guide to Chalcogen-Nitrogen Chemistry, World Scientific, Singapore (2005) 60-63.

[20] J. Konu, T. Chivers, H. M. Tuononen, Inorg. Chem. 45 (2006) in press.

[21] J. Novosad, K. W. Törnroos, M. Necas, A. M. Z. Slawin, J. D. Woollins, S. Husebye, Polyhedron 18 (1999) 2861.

[22] S.S. Garje, J. S. Ritch, D. J. Eisler, M. Azfaal, P. O’Brien, T. Chivers, J. Mater. Chem. 10 (2006) 966.

[23] S.S. Garje, D. J. Eisler, J. S. Ritch, M. Azfaal, P. O’Brien, T. Chivers, J. Am. Chem. Soc. 128 (2006) 3120.

[24] A. J. Gaunt, B. L. Scott, M. P. Neu, Angew. Chem. Int. Ed. 45 (2006) 1638.

[25] M. C. Copsey, M. Afzaal, T. Chivers, P. O’Brien, Dalton Trans. to be submitted.

[26] J. D. E. T. Wilton-Ely, A. Schier, H. Schmidbaur, Inorg. Chem. 40 (2001) 4656.
[27] M. Azfaal, D. J. Crouch, P. O'Brien, J. Raftery, P. J. Skabara, A. J. P. White, D. J. Williams, J. Mater. Chem. 14 (2004) 233.
[28] T. Chivers, M. Parvez, G. Schatte, Angew. Chem. Int. Ed. 38 (1999) 2217.
[29] D. J. Birdsall, A. M. Z. Slawin, J. D. Woollins, Inorg. Chem. 38 (1999) 4152.
[30] M. C. Copsey, T. Chivers, Chem. Commun. (2005) 4938.
[31] M. C. Copsey, T. Chivers, Unpublished results.
[32] (a) A. M. Z. Slawin, M. B. Smith, J. D. Woollins, J. Chem. Soc. Dalton Trans. (1997) 1877; (b) E. V. Garcia-Baez, M. J. Rosales-Hoz, H. Nöth, I. Haiduc, C. Silvestru, Inorg. Chem. Commun. 3 (2000) 173.
[33] M. Arca, A. Garau, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani, Z. Anorg. Allg. Chem. 625 (1999) 517.
[34] M. C. Kuchta, G. Parkin, Inorg. Chem. 36 (1997) 2492.
[35] W. Uhl, R. Graupner, M. Pohlmann, S. Pohl, W. Saak, Chem. Ber. 129 (1996) 143.
[36] K. Merzweiler, F. Rudolf, L. Brands, Z. Naturforsch. 47B (1992) 470.
[37] H. Rahbarnoohi, R. Kumar, M. J. Heeg, J. P. Oliver, Organometallics 14 (1995) 502.
[38] C. J. Warren, S. S. Dhingra, R. C. Haushalter, A. B. Bocarlsey, J. Solid State Chem. 112 (1994) 340.
[39] S.S. Garje, M. C. Copsey, M. Azfaal, P. O'Brien, T. Chivers, J. Mater. Chem. 10 (2006) in press.
[40] R. J. Baker, C. Jones, Dalton Trans. (2005) 1341.
[41] S.D. Nogai, A. Schier, H. Schmidbaur, Z. Naturforsch. 56B (2001) 711.
[42] P. Pyykkö Chem. Rev. 97 (1997) 597.
[43] P. O'Brien, J. Organomet. Chem. this issue

Captions for Figures

Fig. 1. Molecular structure of $\{Na[TeP^iPr_2NP^iPr_2Te]\}_\infty$ (**3**). A crystallographic inversion centre located at the centre of the Na_2Te_2 rhombus relates atoms with their symmetry equivalents (denoted by the "A" suffix); the extended structure propagates by translation along the *a* axis (denoted with a prime symbol).

Fig. 2. Molecular structures of (a) $(TeP^iPr_2NP^iPr_2Te\text{-})_2$ (**5**); d(Te-Te) = 2.946(1) Å, τ(P-Te-Te-P) = 180 °, (b) $(SPtBu_2NPtBu_2S\text{-})_2$ (**6**); d(S-S) = 2.104(2) Å, τ(P-S-S-P) = 180 °, (c) $(SeP^iPr_2NP^iPr_2Se\text{-})_2$ (**7**); d(Se-Se) = 2.470(1) Å, τ(P-Se-Se-P) = 155 °, and (d) $(SeP^tBu_2NP^tBu_2Se\text{-})_2$ (**8**); d(Se-Se) = 2.464(1) Å, τ(P-Se-Se-P) = 180 °.

Fig. 3. Molecular structure of $(TeP^tBu_2NP^tBu_2Te\text{-})_2$ (**9**); d(Te2-Te3) = 3.102(1) Å, d(Te1-Te2) = 2.981(1) Å, d(Te2-Te4) = 3.253(1) Å, (<Te3-Te2-Te1) = 175.46(3)^o.

Fig. 4. Structural isomers for the dimers $(ER_2PNPR_2E\text{-})_2$ (E = S, Se, Te; R = ^{i}Pr, ^{t}Bu).

Fig. 5. Frontier orbitals of $[(EP^iPr_2)_2N]^+$ (E = Se, Te) ring systems (Reproduced by permission of the Royal Society of Chemistry from *Chem. Commun.*, (2006) 1634).

Fig. 6. Solid-state structures of (a) $[(EP^iPr_2)_2N]I$ (**10b**, E = Se; **10c**, E = Te), (b) $[(EP^tBu_2)_2N]I$ (**11b**, E = Se; **11c**, E = Te), (c) $[(TePPh_2)_2N]I$ (**13c**) and (d) $[(TeP^iPr_2)_2N]Cl$ (**14**).

Fig 7. Molecular structures of (a) $M[Te_2(P^iPr_2)_2N]_2$ (**17a**, M = Zn; **17b**, M = Cd; **17c**, M = Hg), (b) $M[Te_2(P^iPr_2)_2N]_3$ (**18a**, M = Sb; **18b,** M = Bi) and (c) $M[Te_2(P^iPr_2)_2N]_3$ (**19a**, M = La; **19b**, M = U).

Fig. 8. Molecular structure of $(Ph_3P)Au[(TeP^iPr_2)_2N]$ (**20**).

Fig. 9. Molecular structures of (a) $[Ag(TeP^iPr_2)_2N]_6$ (**21**) and (b) $[Ag(TePPh_2)_2N]_4$ (**22**) (only *alpha*-carbon atoms of phenyl and *iso*-propyl groups are shown).

Fig. 10. Structural comparison of (a) $[Cu(TeP^iPr_2)_2N]_3$ (**23c**) and (b) $[Cu(EP^iPr_2)_2N]_3$ (**23a**, E = S; **23b**, E = Se).

Fig. 11. Molecular structure of $\{Me_2Al(TMEDA)][(TeP^iPr_2)_2N]$ (**24**).