Formation of Ga_2Te_2 and M_3Te_3 (M = Ga, In) rings from reactions of sodium ditelluroimidodiphosphinate with Group 13 halides

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Metathetical reactions of $Na[N(^iPr_2PTe)_2]$ with Group 13 metal halides produce the telluride complexes $\{Ga(\mu\text{-}Te)[^iPr_2PN^iPr_2PTe]\}_2$ (2) and $\{M(\mu\text{-}Te)[N(^iPr_2PTe)_2]\}_3$, M = In (3) and Ga (4), which contain central Ga_2Te_2 and M_3Te_3 rings, respectively.

The coordination chemistry of the dichalcogenoimidodiphosphinate ligands **1a** and **1b** has been investigated extensively.[1] A variety of homoleptic Group 13 complexes have been characterized including a spirocyclic gallium cation $[GaL_2]^+$ (L = **1b**, R = Ph),[2] the octahedral indium complex InL_3 (L = **1b**, R = Ph),[3] and the metal–metal bonded species LGa–GaL (L = **1a**, R = Ph).[4] Complexes containing a Group 13 metal linked to a chalcogen have provoked interest as single-source precursors to binary Group 13–Group 16 systems (referred to as III/VI compounds in the materials literature), which have potential applications in optoelectronic and photovoltaic devices.[5] For example, O'Brien and co-workers have demonstrated that organometallic complexes of the type R'_2ML (R' = Me, Et; M = Ga, In; L = **1b**, R = ^iPr) can be used to deposit thin films of M_2Se_3 on glass substrates by employing CVD techniques.[6]

Studies of the analogous tellurium-containing ligand **1c** have been hampered because the approach that is used for the synthesis of **1a** and **1b** is not applicable to the heaviest chalcogen.[1] Three years ago we reported an alternative method which was successful for the preparation of **1c** (R = Ph).[7] More recently, we have extended this synthesis to the more volatile *iso*-propyl derivative **1c** (R = ^iPr) which, as the sodium salt, has been employed in the preparation of the homoleptic complexes ML_2 (M = Zn, Cd, Hg) and ML_3 (M = Sb, Bi) in straightforward metathetical reactions.[8] We have also shown that the one-electron oxidation of **1c** (R = ^iPr) with iodine produces the unusual ditelluride $[TeP^iPr_2N^iPr_2PTe\text{-}]_2$ with a long Te–Te bond, implying that redox transformations may be a complicating feature of metatheses employing the reagent **1c**.[9] In this communication we describe the formation and structures of the Group 13 complexes $\{Ga(\mu\text{-}Te)[^iPr_2PN^iPr_2PTe]\}_2$ (2) and $\{M(\mu\text{-}Te)[N(^iPr_2PTe)_2]\}_3$ (3, M = In; 4, M = Ga) in which the central feature is a four-membered Ga_2Te_2 or six-membered M_3Te_3 ring (M = Ga, In), respectively. This chalcogen transfer from the ligand to the metal centre is unprecedented in the well-studied chemistry of ligands of the type **1**.[1]
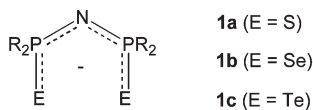
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In an attempt to prepare $GaCl_2[N(^iPr_2PTe)]$, *cf*. $GaCl_2L$ (L = **1a** or **1b**, R = Ph),[2] the metathesis reaction of $Na[N(^iPr_2PTe)_2]$ with an equimolar amount of gallium trichloride was carried out. After filtration to remove sodium chloride, a yellow crystalline product was obtained after storage in a mixture of thf and hexane at −18 °C. A single crystal X-ray diffraction analysis showed the crystalline product to be the dimeric gallium complex $\{Ga(\mu\text{-}Te)[^iPr_2PN^iPr_2PTe]\}_2$ (2) (Fig. 1).†

In contrast to all other metal complexes of ligands of the type **1**,[1] complex **2** does not contain a six-membered metallacycle. Instead, **2** consists of two five-membered PNPTeGa rings linked by two bridging telluride ligands. The molecule lies on an inversion centre with the telluride bridges forming a central, planar Ga_2Te_2 ring, orthogonal to the two five-membered rings. The two PNP(Te) ligands are arranged in a *trans* conformation in the solid state. The observed structure formally arises from transfer of tellurium from the ligand to the metal centre, accompanied by a reduction of one of the phosphorus centres from oxidation state +5 to +3. This change in oxidation state is reflected in the P–N bonds lengths. The P–N bond from the phosphorus(III) centre is slightly elongated at 1.622(3) Å compared to that from the phosphorus(V) centre at 1.594(3) Å.

In comparison to the dichalcogenated species **1**, the co-ordination chemistry of monochalcogeno ligands of the type PR_2NPR_2E (E = S, Se or Te), as observed in complex **2**, is much less developed and the few structurally characterised examples are restricted solely to transition metal complexes.[10–12] Complex **2** is the first metal complex of the mono*telluro*imido-diphosphinate
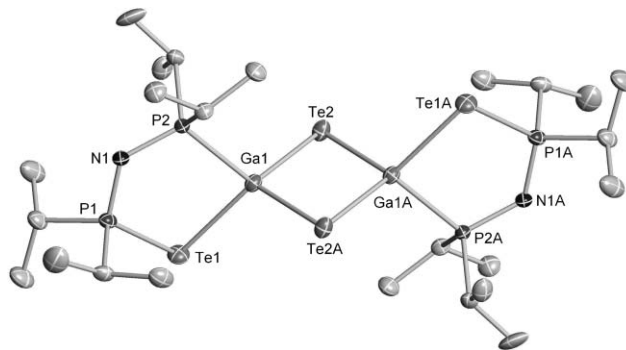

Fig. 1 Molecular structure of **2**; 30% thermal ellipsoids are shown. Hydrogen atoms and lattice thf have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.594(3), P(2)–N(1) 1.622(3), P(1)–Te(1) 2.453(1), P(2)–Ga(1) 2.396(1), Te(1)–Ga(1) 2.653(1), Te(2)–Ga(1) 2.5783(7), P(1)–N(1)–P(2) 126.4(2). Symmetry transformation used to generate equivalent atoms labelled 'A': 2 − x, −y, −z.

ligand, and surprisingly, the first structurally characterised p-block metal complex of the ligand type PR$_2$NPR$_2$E (E = O, S, Se or Te).

The P–Te bond length in **2**, 2.453(1) Å, is comparable to those seen in M[N(^{i}Pr$_2$PTe)$_2$]$_3$, (M = Sb, Bi) which range from 2.431(2)–2.451(4) Å.[8] The bond lengths and bond angles in the Ga$_2$Te$_2$ core (2.5873(7) and 2.5876(7) Å) are very similar to those observed in previously reported Ga$_2$Te$_2$ rings.[13] The Ga(1)–Te(1) co-ordinative bond is slightly longer at 2.653(1) Å. The gallium centre displays the expected distorted tetrahedral geometry. The P–N–P angle of 126.4(2)° in the five-membered ring is substantially smaller than those in the six-membered rings formed by metal complexes of **1c**, 132.0(3)–148.2(3)°. This smaller P–N–P angle is consistent with other five-membered rings in complexes of the monochalcogenoimidodiphosphinate ligands (*cf.* 123.3(4)° and 122.1(5)° in M[PR$_2$NPR$_2$Se]$_2$, M = Pt and M[PR$_2$NHPR$_2$Se]$_2$ M = Pd, respectively).[10]

In order to account for the observed product **2**, we propose that initially a reaction of three equivalents of Na[N(^{i}Pr$_2$Te)$_2$] with one equivalent of GaCl$_3$ occurs to give the octahedral complex Ga[N(^{i}Pr$_2$PTe)$_2$]$_3$. Subsequent reductive elimination of the known ditelluride complex [TeP^{i}Pr$_2$N^{i}Pr$_2$PTe]$_2$ gives the gallium(I) complex Ga[N(^{i}Pr$_2$PTe)$_2$] (Scheme 1). The latter complex then undergoes a tellurium-transfer process to give the gallatellurone Te=Ga[N(^{i}Pr$_2$PTe)$_2$], which dimerizes spontaneously to give **2**. It is well-known that the terminal Ga=Te functionality will behave in such a manner in the absence of kinetic stabilization by bulky

groups.[14] On deliberate reaction of Na[N(^{i}Pr$_2$PTe)$_2$] with GaCl$_3$ in a 3 : 1 molar ratio, one equivalent of the ligand is observed to form complex **2** in 48% yield. The remaining 2 equivalents are isolated as the ditelluride [TeP^{i}Pr$_2$N^{i}Pr$_2$PTe]$_2$ complex (approx. 90% yield) consistent with the formation of **2** by the proposed redox process.

Analysis by NMR spectroscopy suggests that the dimeric structure of **2** is retained in solution. The ^{31}P{^{1}H} NMR spectrum in d$_8$-thf shows two sets of two doublets (ratio 1.00 : 0.42), each with a two-bond phosphorus coupling of 29 Hz. The similarity of the chemical shifts and identical coupling constants suggests the presence of *trans* (**2a**) and *cis* (**2b**) isomers in solution (Scheme 1). We tentatively assign the major species as the crystallised isomer **2a**.

In order to probe the unexpected reactivity of the ligand **1c** further, the reaction of Na[N(^{i}Pr$_2$PTe)$_2$] with InCl$_3$ in a 1 : 1 molar ratio in thf was attempted. The ^{31}P NMR spectrum of the reaction solution showed multiple peaks suggesting a variety of products. Concentration of this solution and storage at −18 °C for several days yielded a small crop of yellow block crystals. Analysis of the yellow crystalline product by low temperature X-ray diffraction showed this complex to be {In(μ-Te) [N(^{i}Pr$_2$PTe)$_2$]}$_3$ (**3**) (Fig. 2).† Complex **3** consists of three six-membered InTePNPTe rings linked together by three telluride bridges, forming a central (InTe)$_3$ ring which has a distorted boat-shaped structure. Several different architectures have previously been observed, including cubes,[15,16] *seco*-cubes[17] and four-membered rings[18,19] but to our knowledge, this is a new structural motif for InTe-containing compounds. The structural parameters of the ligand are consistent with those observed in previous metal complexes of **1c** (R = ^{i}Pr).[8] The In–Te bonds outside of the central ring (exocyclic) are significantly longer at 2.8089(9) Å than the endocyclic bond lengths of 2.744(1) Å. However, both fall within the range previously observed for In–Te bonds.[15–19]

The reaction pathway to the formation of **3** is unclear, however, significant quantities of the ditelluride complex, [TeP^{i}Pr$_2$N^{i}Pr$_2$PTe]$_2$, are also produced in this reaction. Complex
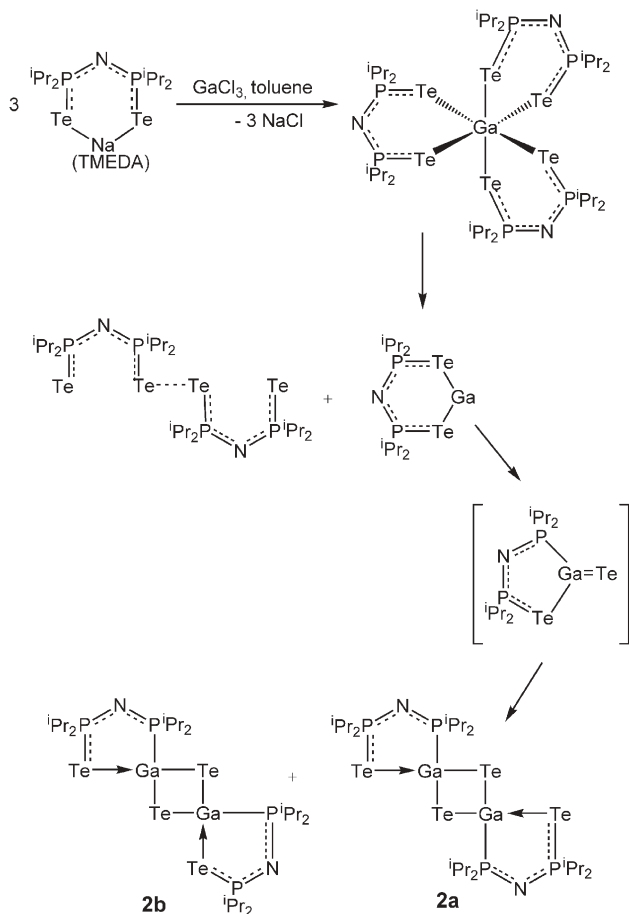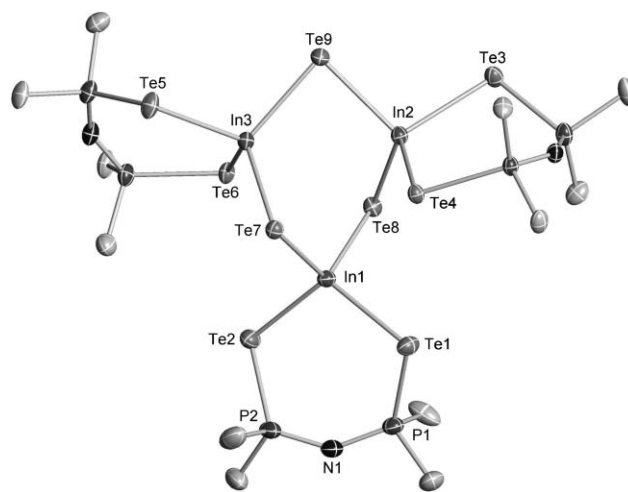
Fig. 2 Molecular structure of **3**; 30% thermal ellipsoids are shown. Lattice solvent, hydrogen atoms and methyl carbons have been omitted for clarity. Selected mean bond lengths (Å) and angles (°): P–N 1.587(7), P–Te 2.450(2), In–Te$_{endo}$ 2.744(1), In–Te$_{exo}$ 2.8089(9); P–N–P 145.1(5), P–Te–In 99.86(6), Te$_{exo}$–In–Te$_{exo}$ 90.07(3), Te$_{endo}$–In–Te$_{endo}$ 113.25(3), Te$_{endo}$–In–Te$_{exo}$ 108.71(3).

Scheme 1

3 can be obtained in a higher yield (75%) from the reaction of In(I)Cl and Na[N(^{i}Pr$_2$PTe)$_2$], in the presence of elemental tellurium, in thf at 60 °C for 18 h.‡ This route allows the isolation of pure **3**, without contamination by other products.

The ternary compounds GaSeBr and GaSBr, recently synthesized by Schmidbaur *et al.*, form soluble adducts with various pyridine ligands that contain six-membered Ga$_3$E$_3$ (E = S, Se) rings.[20] However, the Ga$_3$Te$_3$ ring system is apparently unknown. Consequently, we investigated the reaction of Na[N(^{i}Pr$_2$PTe)$_2$] and "GaI",[21] in the presence of tellurium, in an attempt to form a gallium analogue of **3**.‡ A yellow solid was obtained from this reaction and analysed by NMR spectroscopy (^{1}H and ^{31}P), CHN analysis and single crystal X-ray diffraction.†This confirmed that the product was {Ga(μ-Te) [N(^{i}Pr$_2$PTe)$_2$]}$_3$ (**4**).

Examination of the solid-state structure of **4** shows it to be isostructural with **3** (Fig. 2). The Ga–Te bonds which make up the six-membered ring are significantly shorter (mean 2.582(2) Å) than those which co-ordinate the ligand **1c** (R = ^{i}Pr) to the metal centre (mean 2.657(2) Å). These bond lengths are almost identical to those observed in complex **2**, which contains the four-membered Ga$_2$Te$_2$ ring.

In summary, the tellurium-transfer reaction of **1c** (R = ^{i}Pr) reported in this communication represents a new aspect of the chemistry of dichalcogenoimidodiphosphinate complexes. Compounds **3** and **4** contain the first examples of six-membered rings of the type M$_3$Te$_3$ (M = In and Ga). The juxtaposition of several metal and tellurium sites makes **3** and **4** worthy candidates for investigation as single-source precursors to thin films of binary Group 13 tellurides. This aspect of their chemistry is being pursued.

Notes and references

† Crystal data for **2**: C$_{32}$H$_{72}$Ga$_2$N$_2$O$_2$P$_4$Te$_4$, *M* = 1290.64, monoclinic, *P*2$_1$/*n*, *a* = 13.478(3) , *b* = 8.493(2), *c* = 21.060(4) Å, *β* = 94.42(3)°, *V* = 2403.4(8) Å^3, *Z* = 2, *T* = 173(2) K, *D* = 1.783 g cm^{-3}, *μ*(Mo-K*α*) = 3.661 mm^{-1}, *R* = 0.0301 and *wR* = 0.0648 (all data). For **3**: C$_{39}$H$_{90}$In$_3$N$_3$O$_{0.75}$ P$_6$ Te$_9$, *M* = 2291.82, monoclinic, *P*2$_1$/*c*, *a* = 16.423(3), *b* = 17.204(3), *c* = 27.475(6) Å, *β* = 90.31(3)°, *V* = 7763(3) Å^3, *Z* = 4, *T* = 173(2) K, *D* = 1.961 gcm^{-3}, *μ*(Mo-K*α*) = 4.348 mm^{-1}, *R* = 0.0454 and *wR* = 0.1206 (all data). For **4**: C$_{40}$H$_{92}$Ga$_3$N$_3$OP$_6$Te$_9$, *M* = 2174.55, triclinic, *P*-1, *a* = 13.634(3), *b* = 16.349(3), *c* = 16.396(3) Å, *α* = 78.16(3)°, *β* = 85.85(3)°, *γ* = 79.27(3)°, *V* = 3512(1) Å^3, *Z* = 2, *T* = 173(2) K, *D* = 2.056 g cm^{-3}, *μ*(Mo-K*α*) = 4.972 mm^{-1}, *R* = 0.0523 and *wR* = 0.1205 (all data). Structures of **2**, **3** and **4** all contain poorly ordered lattice thf molecules. In all cases, the C–C, C–O and cross-molecule distances in the thf rings have been fixed to reasonable values and refined. Structures **3** and **4** both contain disordered thf molecules which have been split over several positions and refined with appropriate occupancies as determined by the respective *U* values. CCDC 278063, 278064 and 278065. See http://dx.doi.org/10.1039/b510342h for crystallographic data in CIF or other electronic format.

‡ **Synthesis of {Ga(μ–Te)[^{i}Pr$_2$PNP^{i}Pr$_2$Te]}$_2$ (2).** Compound **2** was obtained from the reaction of Na[N(^{i}Pr$_2$PTe)$_2$]·TMEDA (1.928 g, 3.00 mmol) with GaCl$_3$ (0.176 g, 1.00 mmol) in toluene. The dark red solution was filtered to remove NaCl and the toluene removed *in vacuo*. Dissolution in the minimum amount of thf and hexane and storage at −18 °C yielded yellow needle crystals (0.275 g) Yield 48%, mp 144–147 °C. NMR data (C$_4$D$_8$O, 25 °C) ^{1}H: 2.57–2.36 (m, 4H, –C*H*(CH$_3$)$_2$), 2.24–2.17 (m, 4H, –C*H*(CH$_3$)$_2$), 1.43–1.28 (m, 24H, –CH(C*H*$_3$)$_2$), 1.20–1.06 (m, 24H, –CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} *δ* 83.1 (d, $^1J_{\mathrm{P,Te}}$ 1094 Hz, $^2J_{\mathrm{P,P}}$ 30 Hz), 82.1 (d, $^1J_{\mathrm{P-125Te}}$ 1094 Hz, $^2J_{\mathrm{P,P}}$ 29 Hz), 49.0 (d, $^2J_{\mathrm{P,P}}$ 29 Hz), 47.3 (d, $^2J_{\mathrm{P,P}}$ 29 Hz). Anal. Calc. for Ga$_2$Te$_4$P$_4$N$_2$C$_{24}$H$_{56}$ C 25.14, H 4.92, N 2.44; Found C 25.49, H 5.05, N 2.39%. **Synthesis of {In(μ-Te)[^{i}Pr$_2$P(Te)NP(Te)^{i}Pr$_2$]}$_3$ (3).** A solution of Na[^{i}Pr$_2$P(Te)NP(Te)^{i}Pr$_2$]·TMEDA (0.642 g, 1.00 mmol) in thf (15 mL) was added to a slurry of InCl (0.150 g, 1.00 mmol) and tellurium (0.128 g, 1.00 mmol) in thf (15 mL). The reaction was stirred at 60 °C for 18 h. The reaction mixture was filtered to remove unreacted tellurium, producing a clear yellow solution. Removal of solvent and washing with *n*-hexane yielded a yellow precipitate (0.56 g). Yellow block crystals were grown from a thf solution layered with *n*-hexane at 25 °C after several hours. Yield 75%, 150–153 °C. NMR data (C$_4$D$_8$O, 25 °C) ^{1}H: *δ* 2.19–2.11 (m, 4H –C*H*(CH$_3$)$_2$), 1.32–1.16 (m, 24H –CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} *δ* 34.6 (s, $^1J_{\mathrm{P-125Te}}$ 1210 Hz). Anal. Calc. for In$_3$Te$_9$P$_6$N$_3$C$_{44}$H$_{100}$O$_2$ C 22.19, H 4.23, N 1.76; Found C 22.32, H 4.27, N 1.67%. **Synthesis of {Ga(μ-Te)[^{i}Pr$_2$P(Te)NP(Te)^{i}Pr$_2$]}$_3$ (4).** Prepared in a similar manner to **3**, by using GaI in toluene instead of InCl. Yield 0.224 g 32%, mp 126–129 °C. NMR data (C$_4$D$_8$O, 25 °C) ^{1}H: *δ* 2.23–2.12 (m, 4H, –C*H*(CH$_3$)$_2$), 1.36–1.16 (m, 24H –CH(C*H*$_3$)$_2$). ^{31}P: *δ* 38.9 (s, $^1J_{\mathrm{P-125Te}}$ 1230 Hz). Anal. Calc. for Ga$_3$Te$_9$P$_6$N$_3$C$_{36}$H$_{84}$(C$_4$H$_8$O)$_2$: C 23.52, H 4.49, N 1.87; Found C 23.38, H 4.60, N 1.87%.

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