Gold complexes of ditelluridoimidodiphosphinate ligands — Reversible oxidation of Au(I) to Au(III) via insertion of gold into a phosphorus–tellurium bond[1]

Dana J. Eisler, Stuart D. Robertson, and Tristram Chivers

Abstract: The reaction of (THT)AuCl with (TMEDA)Na[N(TePR$_2$)$_2$] (R = Ph, *i*-Pr, *t*-Bu) produces a series of gold (III) complexes of the type [{R$_2$PNP(Te)R$_2$}Au(μ-Te)]$_2$ (**4a**, R = *i*-Pr; **4b**, R = Ph; **4c**, R = *t*-Bu) rather than the expected homoleptic Au(I) complexes of the ditelluridoimidodiphosphinate ligands. A combination of solution- and solid-state NMR studies shows that both cis and trans isomers of **4a**–**4c** are formed in these reactions. X-ray structural determinations of the trans isomers of **4a**–**4c** reveal a centrosymmetric arrangement with a central four-membered Au$_2$Te$_2$ ring formed by the formal insertion of gold into a P–Te bond; this insertion process was shown to be reversible upon addition of PPh$_3$ to **4a** to give the monomeric gold(I) complex Ph$_3$PAu[N{TeP(*i*-Pr)$_2$}$_2$]. The X-ray structure of *cis*-**4b** is also described.

Key words: gold, tellurium, redox, X-ray structures, imidodiphosphinate.

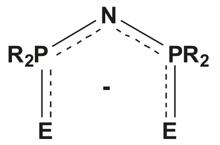
Résumé : La réaction du (THT)AuCl avec le (TMEDA)Na[N(TePr$_2$)$_2$] (R = Ph, *i*-Pr et *t*-Bu) conduit à la formation d'une série de complexes d'or(III) du type [{R$_2$PNP(Te)R$_2$}Au(μ-Te)]$_2$ (**4a**, R = *i*-Pr; **4b**, R = Ph; **4c**, R = *t*-Bu) plutôt qu'aux complexes homoleptiques Au(I) des ligands ditelluridoimidodiphosphinate. Une combinaison d'études RMN en solution et à l'état solide a permis de montrer que dans ces réactions il y a formation des isomères cis- et trans- des produits **4a**–**4c**. Des déterminations de structures par diffraction des rayons X des isomères trans- des produits **4a**–**4c** indiquent qu'ils existent dans un arrangement centrosymétrique, avec un cycle central à quatre membres de Au$_2$Te$_2$ obtenu par l'insertion formelle d'or dans la liaison P-Te; on a démontré que ce processus d'insertion est réversible par addition de PPh$_3$ au produit **4a** qui conduit à la formation du complexe monomère d'or(I), Ph$_3$PAu[N{TeP(*i*-Pr)$_2$}$_2$]. On décrit aussi la structure du produit *cis*-**4b** telle que déterminée par diffraction des rayons X.

Mots-clés : or, tellure, redox, structures déterminées par diffraction des rayons X, imidodiphosphinate.

[Traduit par la Rédaction]

Introduction

Prior to 2002, the chemistry of dichalcogenidoimidodiphosphinate ligands of the type **1** was restricted to derivatives in which E = O, S, or Se. A number of uses or potential uses for metal complexes of these inorganic analogues of acetylacetonates have been identified in review articles (1–3), e.g., as luminescent materials or lanthanide shift reagents, as well as in metal extraction processes. In the last 5–6 years, a renaissance of the interest in such metal complexes has occurred as a result of (*i*) extensive studies by O'Brien and co-workers, which have demonstrated that metal complexes of the selenium analogue of **1a** are suitable single-source precursors for the deposition of pure thin films of metal selenides by using CVD techniques (4) and (*ii*) the discovery of a synthesis of alkali-metal derivatives of the ditellurido derivatives **1a**–**1c** (5–7). The latter development has opened the door to investigations of the fundamental chemistry of these tellurium-containing ligands, as well as applications of their metal complexes as single-source precursors for binary metal tellurides that are of interest for use, inter alia, in solar cells (CdTe, HgTe) or infrared detectors (SnTe), and as thermoelectric materials (Sb$_2$Te$_3$, Bi$_2$Te$_3$) (8).



1a (E = Te, R = *i*-Pr)

1b (E = Te, R = Ph)

1c (E = Te, R = *t*-Bu)

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Dedicated to Professor Dick Puddephatt in recognition of his outstanding contributions to chemistry in Canada.

D.J. Eisler, S.D. Robertson, and T. Chivers.[2] Department of Chemistry, University of Calgary, Calgary, AB T2N 1N4, Canada.

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[2] Corresponding author (e-mail: chivers@ucalgary.ca).

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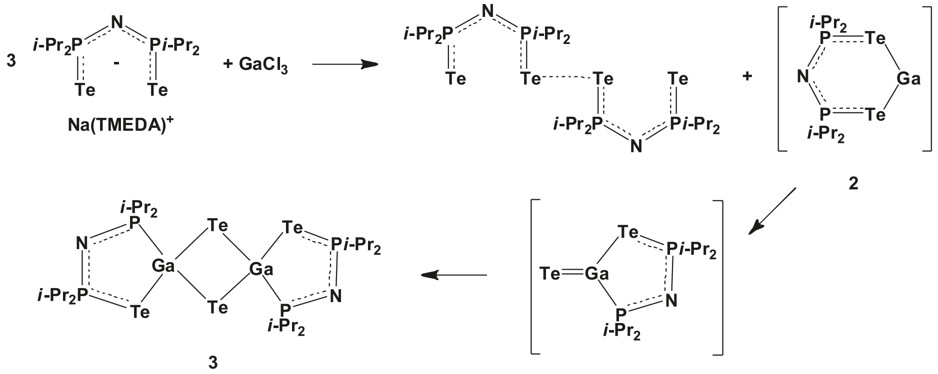
Scheme 1.



Investigations of the redox behaviour of **1a** revealed new aspects of the well-studied chemistry of dichalcogenidoimidodiphosphinate ligands in which one-electron oxidation with iodine produces the dimeric ditelluride $TePR_2NR_2PTe–TePR_2NPR_2Te$ (**2**: R = *i*-Pr) (see Scheme 1) with an elongated central tellurium–tellurium bond (9). Similar dichalcogenides are also obtained upon oxidation of the disulfido and diselenido ligands (**1**: E = S, R = *t*-Bu; E = Se, R = *i*-Pr, *t*-Bu) (7). In the case of **1c**, however, a structural isomer comprised of a contact ion pair in which a $[(TeP\text{-}t\text{-}Bu_2)_2N]^-$ anion is Te, Te chelated to one Te atom of an incipient cyclic cation $[(TeP\text{-}t\text{-}Bu_2)_2N]^+$ is obtained (7). The five-membered cations $[(EPR_2)_2N]^+$ (E = S, Se, Te; R = *i*-Pr, *t*-Bu) are obtained, as iodide salts, by two-electron oxidation of the corresponding anions with iodine (7, 10).

Homoleptic complexes of **1a** with group 12 (Zn, Cd, Hg) and group 15 (Sb, Bi) metals are obtained via metathesis with the appropriate metal halide (6), and the cadmium and antimony complexes have been shown to be effective single-source precursors for pure CdTe (11) and Sb_2Te_3 (12) thin films, respectively, using the technique of aerosol-assisted chemical vapour deposition (AACVD) (8). Homoleptic complexes may also be prepared for coinage metals, although the ditellurido ligands **1a** and **1b** give rise to higher oligomers with silver(I) (specifically, a hexamer for **1a** and a tetramer for **1b**) (13) compared to the trimeric complexes observed for **1** (E = S, Se; R = *i*-Pr) (14). Interestingly, the ditellurido ligands in both copper(I) and silver(I) complexes exhibit the ability to act as doubly bridging ligands, a feature that brings two metal centres in close proximity suggesting the possibility of metallophilic (d^{10}–d^{10}) interactions. The strong reducing power of **1a** is evident in the reaction of the sodium salt with AuCl, which immediately deposits a gold mirror; however, this reduction may be pre-empted by the addition of PPh_3, leading to the isolation of the monomeric gold(I) complex $Ph_3PAu[N\{TeP(i\text{-}Pr)_2\}_2]$ (13). Although tellurium occurs in combination with gold in certain minerals (e.g., krennerite, $AuTe_2$), only a few gold–tellurium complexes have been structurally characterized. Some representative examples include the ternary gold tellurium halides AuTeI (15) and $AuTe_2X$ (X = Cl, I) (16), the tetrameric gold(I) tellurolate $Au_4[TeC(SiMe_3)_3]_4$ (17), the monomeric gold(I) tellurolate $Ph_3PAu[TeC(SiMe_3)_3]$ (17), and a variety of binary gold–tellurium anions, e.g. $Au_4Te_4^{4-}$ (18), $Au_3Te_4^{3-}$ (19), and $AuTe_7^{3-}$ (20).

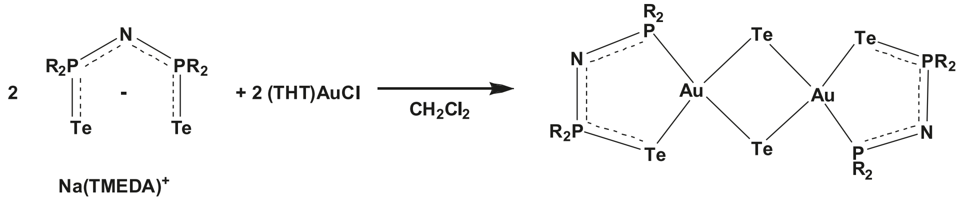
Another fascinating difference between the behaviour of the ditellurido ligand **1a** and the dithio or diselenido analogues (**1**: E = S, Se; R = *i*-Pr) is observed in the reactions with group 13 dihalides (21). For example, the reaction of $GaCl_3$ with 3 equiv. of Na(TMEDA)**1a** produces the dimeric complex $\{Ga(\mu\text{-}Te)[i\text{-}Pr_2P(Te)NPi\text{-}Pr_2]\}_2$ (3) as a mixture of cis and trans isomers, together with a high yield of the ditelluride **2**. As indicated in Scheme 1, the formation of the four-membered Ga_2Te_2 ring in **3** was proposed to occur via initial formation of the homoleptic gallium(III) complex $Ga[N\{TeP(i\text{-}Pr)_2\}]_3$, followed by reductive elimination and formation of the gallium(I) complex $Ga[N\{TeP(i\text{-}Pr)_2\}]$ (**2**). Subsequent rearrangement of this Ga(I) complex to the corresponding gallatellurone followed by dimerisation gives **3** in which the gallium centres are P, Te-chelated by the monotellurido $[TePR_2PNPR_2]^-$ (R = *i*-Pr) ligand. The synthesis of the lithium derivative of this anion and its use as an in situ reagent for the preparation of homoleptic complexes of group 12 metals has been reported recently (22).

To determine whether a more labile two-electron donor than PPh_3 would allow the formation of oligomeric gold complexes of ditelluridoimidodiphosphinate ligands similar to those observed for Cu(I) and Ag(I) (13), we have investigated the reactions of the sodium salts of **1a–1c** with the soluble gold(I) complex (THT)AuCl (THT = tetrahydrothiophene). Interestingly, these reactions give rise to the formation of the gold (III) complexes $[\{R_2PNP(Te)R_2\}Au(\mu\text{-}Te)]_2$ (**4a**, R = *i*-Pr; **4b**, R = Ph; **4c**, R = *t*-Bu) rather than the expected homoleptic Au(I) complexes of **1a–1c**. The characterisation of these new gold(III) complexes in the solid state by X-ray structural determinations and ^{31}P NMR spectroscopy (**4a**) and in solution by multinuclear (^1H, ^{31}P, and ^{125}Te) NMR spectroscopy is discussed.

Results and discussion

The 1:1 reaction of the ditelluridoimidodiphosphinate anions **1a**–**1c**, as their sodium salts, with (THT)AuCl proceeds rapidly in dichloromethane at room temperature producing deeply coloured solutions of the gold complexes **4a**–**4c**, as depicted in Scheme 2. While the *iso*-propyl complex **4a** is moderately soluble in THF and CH_2Cl_2, the phenyl and *tert*-butyl derivatives **4b** and **4c** exhibit poor solubility in common organic solvents. The complexes **4a**–**4c** were all obtained in high purity as crystalline solids, which are stable to

Scheme 2.



4a (R = *i*-Pr) **4b** (R = Ph) **4c** (R = *t*-Bu)

light, air, and moisture in the solid state, but decompose slowly (weeks) in solution at room temperature. The purity of the bulk crystalline samples was confirmed in each case by elemental analysis.

X-ray diffraction studies were carried out on crystalline samples of all three complexes **4a**–**4c**. The most significant difference between the structures involves the substituents on the phosphorus centres, and so the structure of *trans*-**4b** is shown in Fig. 1 as a representative example; a selection of geometrical parameters is given in Table 1. In each case, it was found that the complexes adopt a dimeric structure, which is comprised of a central $[Au_2Te_2]^{2+}$ four-membered ring bound to two monotelluridoimidodiphosphinate anions $[R_2P(Te)NPR_2]^-$ (22) that are arranged in a trans fashion (Fig. 1). A similar structure has been observed previously in the gallium complex **3** (Scheme 1), although in that case, the metal centres are tetrahedral, whereas the gold centres in the complexes **4a**–**4c** are approximately square-planar.

The solid-state structures of the complexes **4a**–**4c** clearly indicate that the gold centres have been oxidized from Au(I) to Au(III). This oxidation formally involves insertion of Au(I) into a phosphorus–tellurium bond of the ditelluridoimidodiphosphinate ligand, with concomitant reduction of one of the P(V) centres to P(III). Oxidation of Au(I) to Au(III) with reagents such as alkyl halides and halogens is well-documented and known to be facile (23). Oxidation by chalcogens has been observed before in the reaction of AuCN with Na_2Se_5, which produced $[Au_2Se_2(Se_4)_2]^{2-}$ (24) containing an Au_2Se_2 ring similar to the central Au_2Te_2 ring observed in the complexes **4a**–**4c**. However, the current work appears to be the only example of the oxidation of Au(I) to Au(III) by insertion into a phosphorus–chalcogen bond. The formation of the Au_2Te_2 ring in **4a**–**4c**, presumably via the initial production of a gold(I) complex of **1a**–**1c**, parallels the transformation depicted in Scheme 1 for the generation of a Ga_2Te_2 ring, except that the Ga(I) complex is generated by reductive elimination rather than an initial metathesis.

Fig. 1. Thermal ellipsoid diagram of complex *trans*-**4b**. Hydrogen atoms have been removed for clarity. Symmetry transformations used to generate equivalent atoms: –*x*, –*y*, –*z*.

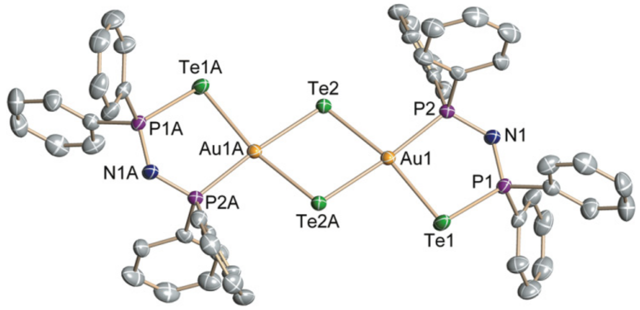


Table 1. Selected bond distances and angles for *trans*-**4a**, *trans*-**4b**, and *trans*-**4c**.

	trans-**4a**	*trans*-**4b**	*trans*-**4c**
Distances [Å]			
Au1—P2	2.365(3)	2.357(2)	2.377(2)
Au1—Te1	2.625(1)	2.6197(8)	2.6267(9)
Au1—Te2	2.628(1)	2.6149(8)	2.649(1)
Au1—Te2A	2.644(1)	2.6446(9)	2.6334(8)
P1—Te1	2.456(3)	2.464(2)	2.474(2)
P1—N1	1.588(8)	1.583(5)	1.589(6)
P2—N1	1.630(7)	1.621(5)	1.634(6)
Te2—Te2A	3.330(8)	3.352(7)	3.2067(9)
Angles [°]			
P2–Au1–Te1	93.82(7)	92.14(4)	94.91(6)
P2–Au1–Te2	98.95(7)	97.43(4)	104.66(6)
Te1–Au1–Te2A	88.82(4)	91.85(3)	85.49(4)
Te2–Au1–Te2A	78.34(4)	79.18(2)	74.75(4)
P2–Au1–Te2A	177.23(6)	173.79(4)	176.96(5)
Te1–Au1–Te2	166.05(3)	168.43(2)	160.02(2)
Au1–Te2–Au1A	101.66(3)	100.82(2)	105.25(2)

As expected for Au(III) (d^8 configuration), the geometry at the gold centres is square-planar, although there are significant deviations from the ideal 90° angles, which likely arise from the softness of the Au–P and Au–Te bonds (Table 1). Regardless of the deviation from the ideal angles, the sum of the bond angles is near 360° for all three complexes (*trans*-**4a**, 359.93°; *trans*-**4b**, 360.60°; *trans*-**4c**, 359.81°). In each case, the most acute angle is the endocyclic Te(2)–Au(1)–Te(2A) angle [*trans*-**4a**, 78.34(4)°; *trans*-**4b**, 79.18(2)°; *trans*-**4c**, 74.75(4)°], while the widest angles are those involving P(2)–Au(1)–Te(2) [*trans*-**4a**, 98.95(7)°; *trans*-**4b**, 97.43(4)°; *trans*-**4c**, 104.66(6)°]. The increase in this latter angle, and compression of the former angles, correlates with an increase in the bulk of the substituents on the phosphorus centres, and may arise from unfavourable steric interactions between these groups and the central Au_2Te_2 ring. The Au–Te–Au angles in the planar four-membered Au_2Te_2 ring in *trans*-**4a**–**4c** are larger than the corresponding Te–Au–Te angles by 23.3–30.5° leading to transannular distances of 3.20–3.35 Å that are well within the sum of van der Waals radii for two tellurium atoms (4.40 Å). For comparison, the Te—Te separation in the four-

Fig. 2. Thermal ellipsoid diagram for one of the two crystallographically independent molecules of the complex *cis*-**4b**. Hydrogen atoms have been removed for clarity.

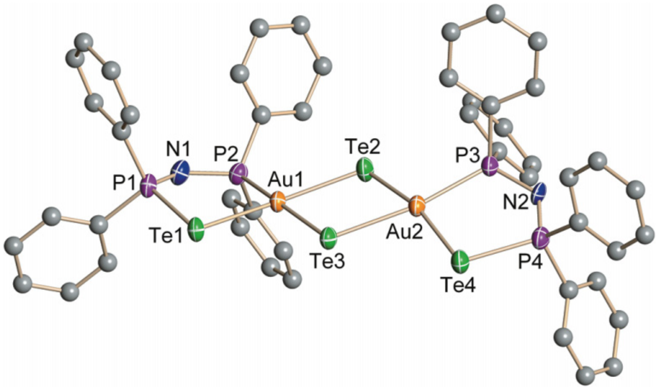


Table 2. Selected bond distances and angles for *cis*-**4b**, molecule **1**.

Distances [Å]	
Au1—P2	2.345(4)
Au1—Te1	2.627(2)
Au1—Te3	2.645(1)
Au2—Te3	2.655(2)
P1—Te1	2.458(5)
P1—N1	1.58(2)
P3—N2	1.60(1)
Te2—Te3	3.347(2)
Au2—P3	2.357(5)
Au1—Te2	2.612(2)
Au2—Te2	2.620(2)
Au2—Te4	2.634(2)
P4—Te4	2.461(5)
P2—N1	1.61(2)
P4—N2	1.61(2)
Angles [°]	
P2–Au1–Te1	93.3(1)
P2–Au1–Te2	98.1(1)
Te1–Au1–Te3	90.73(5)
Te2–Au1–Te3	78.60(5)
Te2–Au1–Te1	166.40(4)
P2–Au1–Te3	173.8(1)
Au1–Te2–Au2	100.23(4)
P3–Au2–Te–4	92.8(1)
P3–Au2–Te2	96.2(1)
Te3–Au2–Te4	93.77(5)
Te2–Au2–Te3	78.28(5)
Te2–Au2–Te4	166.67(5)
P3–Au2–Te3	171.4(1)
Au1–Te3–Au2	102.03(5)

membered Au_2Te_2 rings in AuTeI is 3.235 Å (15). The Au—Te bond lengths fall in a very narrow range for all three complexes [2.6149(8)–2.649(1) Å] and are similar to other reported Au–Te distances (14–20).

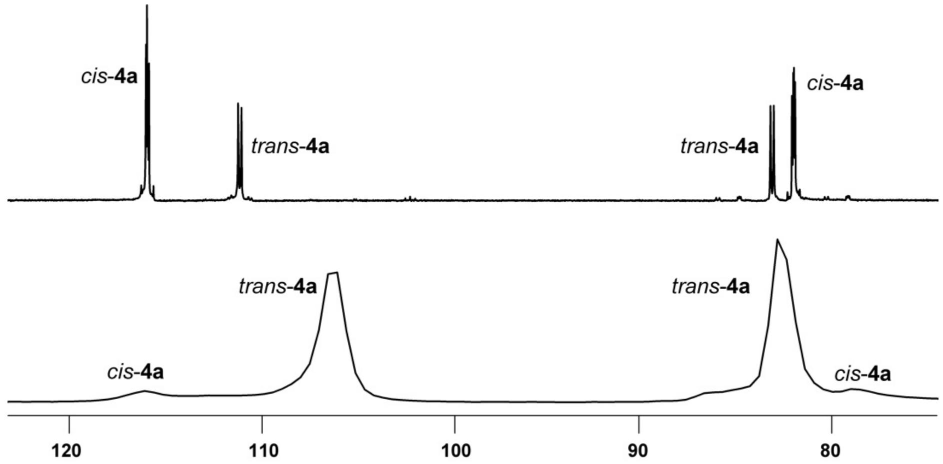
During this work, it was found that rapid crystallization of **4b** from concentrated THF or CH_2Cl_2 solutions resulted in the formation of two distinct crystal morphologies: deep red, rhombohedral plates and orange rectangular plates, the latter of which were identified as *trans*-**4b** by determination of the unit cell. An X-ray crystallographic study on a rhombohedral plate revealed the presence of the cis isomer of complex **4b** (Fig. 2). There are two crystallographically independent, but chemically equivalent, molecules of *cis*-**4b** present in the asymmetric unit, which have very similar metrical parameters.

The geometrical parameters of *cis*-**4b** are similar to those observed for *trans*-**4b**. The geometry of the gold(III) centres is best described as distorted square-planar, with significant deviations from the ideal 90° bond angles (Table 2). The most compressed angles are those contained within the central Au_2Te_2 ring [Te2–Au1–Te3, 78.60(5)°; Te2–Au2–Te3, 78.28° (5)], while the widest angles are P2–Au1–Te2, 98.1(1)° and P3–Au2–Te2, 96.2(1)°. The Au–Te bond distances [range: 2.612(2)–2.655(2) Å] are similar to those observed in the trans complexes of **4a**–**4c**. Like the trans complexes of **4a**–**4c**, the four-membered Au_2Te_2 ring of *cis*-**4b** is planar, with the Au–Te–Au bond angles more than 20° larger than the Te–Au–Te angles. As a consequence, the transannular Te–Te distance is 3.35 Å, which is virtually identical to that of *trans*-**4b**. Regardless of the similarity between the cis and trans structures, there is a clear preference in the solid state for the trans isomer. Slow crystallization of all of the complexes **4a**–**4c** consistently resulted in the isolation of the trans isomer in the solid state; only a single crystal morphology was observed and random testing of multiple crystals from each sample using X-ray crystallography provided exclusively the unit cell for the trans isomer. All attempts to isolate crystals of *cis*-**4a** and *cis*-**4c** were unsuccessful.

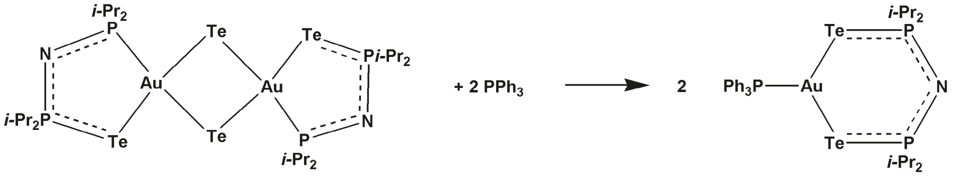
The solution-state NMR spectra obtained for the complexes **4a**–**4c** revealed the presence of two closely related species in solution. For example, in the ^{31}P NMR spectra, two sets of phosphorus resonances, with very similar chemical shifts and coupling constants, were observed in each case. However, the two species were not present in equal quantities, but in a ratio of nearly 2:1 in each case. The observed spectroscopic data can be explained by the presence of both the cis and trans isomers in solution, with one isomer clearly predominating. While it is tempting to assign the resonances of the major component present in solution to the trans isomer, solid-state NMR studies suggest that it is the cis isomer that predominates in solution.

The solid-state ^{31}P NMR spectrum of a crystalline sample of **4a** grown slowly from dichloromethane is compared with the solution-state spectrum in Fig. 3. It is clear from these two spectra that the isomer that predominates in the solid state is, in fact, the minor component present in solution. The unit cell was determined for multiple crystals from this solid-state sample, and in each case the presence of the trans isomer was confirmed. It should be noted that the solid-state ^{31}P NMR spectrum indicates that there is a small quantity of the cis isomer present in the sample. Nonetheless, crystals of the cis isomer could not be detected visually or by crystallographic methods. In contrast, the solid-state ^{31}P NMR spectrum obtained on a sample of **4b** that had been rapidly crystallized showed that the ratio of the two isomers was largely unchanged from that present in solution. This obser-

Fig 3. (Top) Solution ^{31}P NMR spectrum of complex **4a** showing the mixture of cis and trans isomers. (Bottom) Solid-state ^{31}P NMR spectrum (11 kHz) of slowly crystallized **4a**.



Scheme 3.



vation, in conjunction with the relative quantities of crystals of *cis*- and *trans*-**4b** noted in rapidly crystallized samples, also suggests that it is the cis isomer that is the major component in solution. Although it is possible that the trans isomer crystallizes preferentially, leaving the cis isomer in solution, the ^{31}P NMR spectrum obtained for a single crystal of *trans*-**4a** was found to be identical to that of bulk samples of **4a**, with the two sets of resonances in a 2:1 intensity ratio. Thus, it is clear that the cis and trans isomers are readily able to interconvert in solution, although the mechanism by which this occurs is not clear.

Finally, we note a minor difference in the ^{31}P NMR spectra of the cis and trans isomers. The trans isomers exhibit one set of mutually coupled doublets, whereas the resonances for the cis isomers exhibit second-order behaviour and appear as more complex multiplets, as observed for the related square-planar complexes *cis*-[M{Ph$_2$P(E)NPPh$_2$}$_2$] (M = Pd, Pt; E = S, Se) (25).

In light of the facile oxidation of Au(I) to Au(III) observed in this work and the previous observation that Ph$_3$P stabilizes a homoleptic Au(I) complex of **1a** (13), we decided to investigate the reaction of **4a** with Ph$_3$P. Addition of Ph$_3$P to solutions of **4a** resulted in the immediate and quantitative formation of the known complex Ph$_3$PAu[N{TeP(*i*-Pr)$_2$}$_2$] (13), which was identified by ^{31}P NMR spectroscopy (Scheme 3). To further confirm the identity of the complex, it was shown that the addition of an authentic sample of Ph$_3$PAu[N{TeP(*i*-Pr)$_2$}$_2$] to the solution used to obtain the NMR spectrum resulted only in an increase in the intensity of the NMR resonances; no additional resonances were observed.

Conclusions

The reaction of the soluble Au(I) complex (THT)AuCl with the ditelluridoimidodiphosphinate complexes **1a–1c** was found to produce the stable dimeric complexes **4a**–**4c**, in which the gold centres have been oxidized to Au(III). This oxidation involves the formal insertion of the gold centres into a phosphorus–tellurium bond and converts a ditelluridoimidodiphosphinate ligand to a monotelluridoimidodiphosphinate with the formation of an Au$_2$Te$_2$ ring. The insertion of a metal centre into a P–Te bond has been observed previously in the formation of the gallium complex {Ga(μ-Te)[*i*Pr$_2$P(Te)NP*i*Pr$_2$]}$_2$ (3). Taken together, these results indicate that reactions of the ditellurido ligands **1a**–**1c** with metals that have two easily accessible oxidation states, separated by two units, may be complicated by redox chemistry. The reversibility of the redox chemistry that was observed in the current work is unprecedented and may have significant implications in the formation of metal complexes of ditelluridoimidodiphosphinate ligands; in particular, an investigation of the possible occurrence of a similar process for the gallium(III) complex **3** is warranted.

Experimental section

Reagents and general procedures

Solvents were dried and distilled before use: *n*-hexane, THF, and toluene (Na/benzophenone); CH$_2$Cl$_2$ (calcium hydride). The ditelluridoimidodiphosphinate complexes **1a** (6), **1b** (5), and **1c** (7) and the complex (THT)AuCl (26) were prepared according to the literature procedures. The handling of air- and moisture-sensitive materials was performed under an atmosphere of argon gas using standard Schlenk techniques or a glovebox. ^{1}H, ^{31}P, and ^{125}Te NMR spectra were collected using a Bruker AC-300, AMX-300, or DRX-400 spectrometer, and chemical shifts are reported relative to Me_4Si (^{1}H), 85% H_3PO_4 (^{31}P), and Te_2Ph_2 (^{125}Te). Solid-state ^{31}P NMR spectra were collected on a Bruker AM300 wide-bore spectrometer in a 4 mm tube, and chemical shifts are reported relative to $(NH_4)H_2PO_4$. The Analytical Services Laboratory of the Department of Chemistry, University of Calgary, provided elemental analyses.

Preparation of [(*i*-Pr$_2$PNP(Te)*i*-Pr$_2$)Au(μ-Te)]$_2$ (4a)

A solution of **1a** (0.200 g, 0.31 mmol) in CH_2Cl_2 (25 mL) was added to a darkened flask containing a solution of (THT)AuCl (0.100 g, 0.31 mmol) in CH_2Cl_2 (15 mL), resulting in the immediate formation of a dark red solution. The mixture was stirred for 15 min and then filtered through Celite. The solution was stored at –30 °C for 72 h giving dark red crystals of **4a**, suitable for X-ray analysis (0.158 g, 0.11 mmol, 73%). ^{1}H NMR (D_8-THF) δ: 2.35 (m $(CH_3)_2CH$, *trans*-**4a**), 2.25 (m, $(CH_3)_2CH$, *cis*-**4a**), 1.23 (m, $(CH_3)_2CH$, *cis*-**4a**, *trans*-**4a**). ^{31}P NMR (D_8-THF) δ: 113.94 (m, *P*Au, *cis*-**4a**), 108.88 (d, $^2J_{PP}$ = 29 Hz, *P*Au, *trans*-**4a**), 80.70 (d, $^2J_{PP}$ = 29 Hz, $^1J_{TeP}$ = 946 Hz, *P*Te, *trans*-**4a**), 79.15 (m, $^1J_{TeP}$ = 948 Hz, *P*Te, *cis*-**4a**). ^{125}Te NMR δ: 292.0 (d, $^1J_{TeP}$ = 950 Hz, P*Te*, *trans*-**4a**), 281.0 (d, $^1J_{TeP}$ = 943 Hz, P*Te*, *cis*-**4a**), –38.4 (s, μ-Te, *trans*-**4a**), –397.4 (s, μ-Te, *cis*-**4a**). Solid-state ^{31}P NMR δ: 116.17 (*P*Au, *cis*-**4a**), 106.15 (*P*Au, *trans*-**4a**), 82.27 (*P*Te, *trans*-**4a**), 78.28 (*P*Te, *cis*-**4a**). Anal. calcd. for $C_{24}H_{56}Au_2N_2P_4Te_4$ (%): C 20.58, H 4.03, N 2.00; found: C 21.06, H, 3.94, N 1.95.

Preparation of [(Ph$_2$PNP(Te)Ph$_2$)Au(μ-Te)]$_2$ (4b)

A solution of **1b** (0.243 g, 0.31 mmol) in CH_2Cl_2 (25 mL) was added to a darkened flask containing a solution of (THT)AuCl (0.100 g, 0.31 mmol) in CH_2Cl_2 (15 mL), resulting in the immediate formation of a dark green solution. The mixture was stirred for 15 min and then filtered through Celite, concentrated to ~15 mL and then stored at –30 °C for 24 h giving crystalline **4b** (0.112 g, 0.07 mmol, 43%). ^{1}H NMR (D_8-THF) δ: 7.69, 7.35 (m, Phenyl-*H*; *cis*-, *trans*-**4b**). ^{31}P NMR (CD_2Cl_2) δ: 78.29 (m, *P*Au, *cis*-**4b**), 70.21 (d, $^2J_{PP}$ = 80 Hz, *P*Au, *trans*-**4b**), 30.41 (m, $^1J_{TeP}$ = 982 Hz, *P*Te, *cis*-**4b**), 30.22 (d, $^2J_{PP}$ = 80 Hz, $^1J_{TeP}$ = 982 Hz, *P*Te, *trans*-**4b**). Anal. calcd. for $C_{48}H_{40}Au_2N_2P_4Te_4$ (%): C 34.46, H 2.41, N 1.67; found: C 34.56, H, 2.19, N 1.61. X-ray quality crystals of *trans*-**4b** were grown by slow evaporation of a solution of the complex in CH_2Cl_2. A suitable crystal for X-ray analysis of the complex *cis*-**4b** was obtained from a concentrated solution of the complex in THF.

Preparation of [(*t*-Bu$_2$PNP(Te)*t*-Bu$_2$)Au(μ-Te)]$_2$ (4c)

A solution of **1c** (0.218 g, 0.31 mmol) in CH_2Cl_2 (30 mL) was added to a darkened flask containing a solution of (THT)AuCl (0.100 g, 0.31 mmol) in CH_2Cl_2 (30 mL), resulting in the immediate formation of a dark red solution. The mixture was stirred for 15 min and then filtered through Celite. The solution was concentrated to ~30 mL and stored at –30 °C for 72 h giving crystalline **4c** (0.080 g, 0.05 mmol, 34%). ^{1}H NMR (CD_2Cl_2) δ: 1.39, (m, $C(CH_3)_3$, *cis*-**4c**), 1.18 (m, $C(CH_3)_3$, *trans*-**4c**). ^{31}P NMR (CD_2Cl_2) δ: 129.17 (m, *P*Au, *cis*-**4c**), 124.14 (d, $^2J_{PP}$ = 27 Hz, *P*Au, *trans*-**4c**), 94.71 (d, $^2J_{PP}$ = 27 Hz, $^1J_{TeP}$ = 980 Hz, *P*Te, *trans*-**4c**), 94.02 (m, $^1J_{TeP}$ = 980 Hz, *P*Te, *cis*-**4c**). Anal. calcd. for $C_{32}H_{72}Au_2N_2P_4Te_4$ (%): C 25.40, H 4.80, N 1.85; found: C 25.43, H, 4.48, N 1.75. X-ray quality crystals of *trans*-**4c** were grown by slow evaporation of a solution of the complex in CH_2Cl_2.

X-ray structural analyses

Crystal data for *trans*-**4a**, *trans*-**4b**, *cis*-**4b**, and *trans*-**4c** are summarized in Table 3.[3] A suitable crystal of the complex was selected, coated in Paratone oil, and mounted on a glass fibre. Data were collected at 173 K (273 K = 0 °C) on a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) via ω and ϕ scans. The unit-cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. After data reduction, the data were corrected for absorption using SORTAV (27). The structures were solved using the automated Patterson routine within SHELXS-97 (28) and refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program (29). The hydrogen atoms were calculated geometrically and were riding on their respective atoms unless otherwise noted. For the complexes *trans*-**4a**, *trans*-**4b**, and *trans*-**4c**, all non-hydrogen atoms were refined with anisotropic thermal parameters. In each case, only one-half of the molecule was located in the difference Fourier map as the molecule is situated around a centre of symmetry. In the case of complex *cis*-**4b**, the crystals diffracted weakly, and so a relatively poor-quality dataset was obtained. The complex crystallizes with two chemically equivalent, but crystallographically independent, molecules in the asymmetric unit. Four of the phenyl substituents were disordered and each was modelled as an isotropic 50:50 mixture with geometric restraints; all other phenyl rings were constrained to be regular hexagons and were refined with isotropic thermal displacement parameters. The lattice-bound THF molecules were poorly ordered, and each was modelled as an isotropic 50:50 mixture with geometric restraints. Due to the low quality of the data, only the Au, Te, P, and N atoms making up the core of the structure were refined with anisotropic thermal displacement parameters.

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[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3762. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 680164–680167 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 3. Crystallographic data for complexes *trans*-**4a**, *trans*-**4b**, *cis*-**4b**, and *trans*-**4c**.

Crystal	*trans*-**4a**	*trans*-**4b**	*cis*-**4b**	*trans*-**4c**
Empirical formula	$C_{24}H_{56}Au_2N_2P_4Te_4$	$C_{48}H_{40}Au_2N_2P_4Te_4$	$C_{48}H_{40}Au_2N_2P_4Te_4\cdot(C_4H_8O)$	$C_{32}H_{72}Au_2N_2P_4Te_4$
Formula mass	1400.92	1673.03	1745.14	1513.13
Colour, habit	Red, block	Orange, plate	Red, plate	Orange, plate
Crystal size (mm)	0.14 × 0.14 × 0.08	0.08 × 0.06 × 0.04	0.10 × 0.08 × 0.04	0.10 × 0.08 × 0.05
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Z	1	1	4	1
a (Å)	8.1864(7)	9.8966(2)	12.1688(3)	8.3382(5)
b (Å)	9.7477(8)	11.0948(3)	19.5417(5)	11.2270(5)
c (Å)	13.901(1)	12.5300(4)	24.6410(6)	13.6625(9)
α (°)	108.625(5)	105.451(2)	108.317(1)	72.509(3)
β(°)	92.495(4)	93.450(2)	90.033(2)	76.957(3)
γ (°)	112.270(3)	110.369(2)	102.362(1)	70.899(3)
Collection ranges	$-9 \le h \le 9$ $-11 \le k \le 11$ $-16 \le l \le 16$	$-12 \le h \le 12$; $-14 \le k \le 14$; $-16 \le l \le 16$	$-12 \le h \le 12$; $-20 \le k \le 20$; $-25 \le l \le 25$	$-10 \le h \le 10$; $-14 \le k \le 14$; $-17 \le l \le 17$
Volume ($Å^3$)	955.49(14)	1225.23(6)	5419.2(2)	1141.13(12)
$D_{calcd.}$ (Mg/m^3)	2.435	2.267	2.139	2.202
μ (mm^{-1})	10.846	8.480	7.675	9.090
F(000)	640	768	3232	704
θ range for data collection (°)	3.15–25.03	2.57–27.50	2.62–21.97	2.76–26.37
Observed reflections	13619	22307	81792	18224
Independent reflections	3349 (R_{int} = 0.092)	5603 (R_{int} = 0.070)	13210 (R_{int} = 0.105)	4659 (R_{int} = 0.093)
Data/restraints/ parameters	3349/0/171	5603/0/271	13210/125/604	4659/0/211
Maximum shift/error	0.00	0.00	0.00	0.00
GooF on F^2	1.046	1.030	1.041	1.035
Final *R* indices $[I > 2\sigma(I)]^a$	0.0440, 0.1005	0.0367, 0.0745	0.0531, 0.1125	0.0445, 0.0983
R indices (all data)^b	0.0598, 0.1089	0.0554, 0.0817	0.0925, 0.1298	0.0703, 0.1106
Largest diff. peak and hole (e $Å^{-3}$)	1.519 and –3.275	1.046 and –2.216	2.194 and –1.953	1.251 and –3.497

$^aR_1 = [\Sigma||F_o|-|F_c||]/[\Sigma|F_o|]$ for $[I > 2\sigma(I)]$.

$^bwR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

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