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Title: New Insights into the Chemistry of Imidodiphosphinates from Investigations of Tellurium-Centered Systems

Year: 2010

Version:

Please cite the original version:

Chivers, T., Ritch, J., Robertson, S., Konu, J., & Tuononen, H. (2010). New Insights into the Chemistry of Imidodiphosphinates from Investigations of Tellurium-Centered Systems. Accounts of Chemical Research, 43(8), 1053-1062. https://doi.org/10.1021/ar900272k

New Insights into the Chemistry of Imidodiphosphinates from Investigations of Tellurium-Centered Systems

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CONSPECTUS

Dichalcogenido-imidodiphosphinates $[N(PR_2E)_2]^-$ (R = alkyl, aryl) are chelating ligands that readily form cyclic complexes with main group or transition metals, as well as lanthanides and actinides. Since their discovery in the early 1960s, the structural chemistry of these metal complexes for E = O, S, Se has been studied extensively and a variety of potential applications have been identified, for example, as NMR shift reagents, luminescent complexes in photonic devices, or single-source precursors for metal sulfides or selenides. A suitable synthesis of the tellurium analogs $[N(PR_2Te)_2]^-$ was not developed until 2002. In the intervening 7 years comprehensive investigations of these tellurium-centered anions, as well as related mixed chalcogen systems, have revealed unanticipated aspects of the fundamental chemistry of these well-established inorganic ligands. An exhaustive examination of previously unrecognized redox behavior has uncovered a variety of novel dimeric arrangements, as well as an extensive series of cyclic cations. In combination with DFT calculations, these new structural frameworks have provided new insights into the nature of chalcogen-chalcogen bonding. Unprecedented structural and reaction chemistry has also been revealed in studies of metal complexes of the ditellurido ligands $[N(PR_2Te)_2]^-$. The large tellurium donor sites confer greater flexibility leading, in some cases, to unique structures in which the tellurium-centered ligand bridges two metal centers. The relatively weak P–Te bonds facilitate metal-insertion reactions (intramolecular oxidative-addition) to give new metal-tellurium ring systems for some group 11 and 13 metals. From a practical perspective, certain metal complexes of the isopropyl-substituted anion $[N(P^iPr_2Te)_2]^-$ serve as suitable single-source precursors for pure metal telluride thin films or novel nanomaterials, e.g. CdTe, PbTe, In_2Te_3, Sb_2Te_3, which have potential applications in solar cells, thermoelectric devices and telecommunications.

1. Introduction

Chalcogen-centered chelating ligands of the type $[N(PR_2E)_2]^-$ (E = O, S, Se; R = alkyl, aryl) [i.e. dichalcogenido(imidodiphosphinates) (PNP)] have a long and venerable history that dates back to the 1960s.[1] In the intervening years many main group and transition-metal complexes have been characterized.[2] Some early potential applications of these complexes included their use as lanthanide shift reagents, in luminescent materials, or in metal-extraction processes.[2a] More recently, renewed interest in this class of compounds has been invigorated by the findings of O'Brien and co-workers that certain metal complexes of the isopropyl derivative $[N(P^iPr_2Se)_2]^-$ are suitable single-source precursors for the production of thin semiconducting films of binary metal selenides, e.g. MSe (M = Zn, Cd, Hg), M_2Se_3 (M = Ga, In, Bi) and PbSe, by using LP-(low-pressure) or AA-(aerosol-assisted) CVD (chemical vapor deposition) techniques.[3] The solvothermal generation of CdSe quantum dots has also been accomplished.[4] In addition to the synthetic challenge of making analogous Te-containing ligands that might display novel chemistry, the prospect of generating novel single-source precursors to metal tellurides excited our interest in this field.

2. Synthesis

The neutral precursors $HN(PR_2E)_2$ (E = S, Se; R = Ph, ^iPr) are readily generated by the direct reaction of the corresponding P^{III}/P^{III} systems $HN(PR_2)_2$ with elemental sulfur or selenium.[5] In the case of tellurium, however, this oxidation is limited to the formation of the yellow monotellurido derivative $TeᶦPr_2PNP(H)ᶦPr_2$ (**1a**),[6] which is isolated as the P–H tautomer in 81 % yield (Scheme 1); the phenyl derivative $HN(PPh_2)_2$ is unreactive towards tellurium.[7] In 2002 we demonstrated that this lack of reactivity can be circumvented by generating the anion $[N(PPh_2)_2]^-$ *prior to the reaction with elemental tellurium*. In this way sodium salts of the ditellurido ligands $[N(PR_2Te)_2]^-$ (**2a**, R = ^{i}Pr;[8] **2a′**, R =Ph;[7] **2a″**, R = ^{t}Bu[9]) are obtained in good yields (Scheme 1). This protocol can be adapted for the synthesis of the mixed chalcogen ligands $[N(P^iPr_2Te)(P^iPr_2E)]^-$ (E = S, Se) (Scheme 1).[10] The best procedure for obtaining the Te/S ligand**,** as the Li derivative **2c,** in high purity (99 %) involves the *in situ* deprotonation of the monotelluride (**1a**) with *n*-butyllithium followed by reaction with sulfur in THF. A similar methodology is employed for the optimal synthesis of the Te/Se reagent **2b** (97 % purity) from the monoselenide (**1b**). The mixed chalcogen anions $[N(P^iPr_2Te)(P^iPr_2E)]^-$ (E = S, Se) can also be obtained as ion-separated cobaltocenium salts by reduction of the corresponding cations (see Section 3.2) with cobaltocene.[11] The "*metallation-first*" approach to these novel tellurium-containing ligands opened the door to a comprehensive investigation of their fundamental chemistry, as well as potential applications of metal complexes as single-source precursors to metal tellurides in the form of thin films or nanomaterials.

3. Redox Behavior

3.1. One-electron Oxidation. In our initial studies we observed that yellow solutions of the monotelluride **1a** become red upon exposure to air and a few crystals of the unusual ditelluride $(TeP^iPr_2N^iPr_2PTe–)_2$ (**4a**) were isolated from the red solution and structurally characterized.[6] This intriguing transformation prompted us to undertake a systematic examination of the redox behavior of the monoanions $[N(PR_2E)_2]^-$ (E = S, Se, Te; R = ^{i}Pr, ^{t}Bu). The one-electron oxidation of their sodium salts with iodine produces the dimers $(EPR_2NR_2PE–)_2$ either in the form of dichalcogenides (DCs) **4a, 4b, 4b′** and **4c′** or as the spirocyclic contact ion pair (CIP) **5a′**.[9] The disulfide **4c** (E = E′ = S; R = ^{i}Pr) could not be obtained owing to hydrogen-abstraction reactions.[9] The availability of the mixed chalcogen anions in **2b** and **2c** provoked the interesting question - which chalcogen-chalcogen bond will be formed preferentially upon one-electron oxidation, E–E, Te–Te or E–Te? Although the oxidation of **2b** and **2c** with I_2 does not proceed cleanly, one-electron reduction of the corresponding cations $[N(P^iPr_2Te)(P^iPr_2E)]^+$ (**6c**, E = Se; **6d**, E = S) with cobaltocene produces the ditellurides **4d** and **4e**; in both cases the dimer with a central Te–Te bond is formed exclusively.[11]

The structures of the DCs **4a, 4b, 4b′, 4c′, 4d** and **4e** all exhibit elongated chalcogen-chalcogen bonds.[9,11] The elongation of the central Te–Te bond in the mixed chalcogen dimers **4d** (ca. 6 %) and **4e** (ca. 3 %) is less pronounced than the value of ca. 8 % for the all-tellurium system **4a**. DFT calculations for the radical $[TeP^iPr_2N^iPr_2PTe]^•$ reveal that the SOMO is comprised of an almost linear combination of tellurium p_x and p_y orbitals (Figure 1). The spatial orientation of monomeric units in the dimer and the multicentered nature of the radical SOMO effectively weaken the Te–Te bonding interaction thus accounting for the elongated Te–Te bond. Consistently, the calculated dimerization energy for the model reaction $2[TePMe_2NMe_2PTe]^• \rightarrow (TePMe_2NMe_2PTe–)_2$ is -80 kJ mol^{-1},[6] cf. D(Te-Te) = 138 kJ mol^{-1} for PhTe–TePh. The attenuation of the Te–Te bond elongation in the mixed chalcogen systems **4d** and **4e** compared to that in **4a** is attributed to the polarization of the SOMO of the neutral radicals $[EP^iPr_2N^iPr_2PTe]^\bullet$ towards the more electropositive tellurium atom when E = S, Se resulting in stronger Te–Te overlap.[11] The elongation of the central chalcogen–chalcogen bond in the diselenides **4b** and **4b′** is ca. 6 % and that in the disulfide **4c′** is only 2 %, suggesting better overlap of the two radical SOMOs for the lighter chalcogens We note, however, that the markedly different conformations of acyclic DCs is likely to be a contributing factor.[9]

DFT calculations of the relative energies of the two structural isomers observed for the symmetrical dimers $(EPR_2NR_2PE–)_2$ (DC and CIP) as a function of (a) the chalcogen and (b) the R group reveal interesting trends.[9] For both the ^{i}Pr and ^{t}Bu series the stability of the CIP increases relative to that of the DC upon going from sulfur to tellurium. However, the CIP is predicted to be significantly more stable in only one case (R = ^{t}Bu, E = Te), consistent with the observed isolation of **5a′**. However, the differences in energy are insignificant in the cases of E = Te, R = ^{i}Pr and E = Se and R = ^{t}Bu. Thus, the preferred structure could be influenced by either (a) the method of synthesis or (b) crystal packing forces.

In this context we were intrigued to prepare and determine the structures of dimers in which the two monomeric units are different, e.g. $(EPR_2NR_2PE–TePR_2NR_2PTe)$ (E = Se, S). The reactions of sodium salts of the acyclic anions $[(TMEDA)NaN(PR_2E)_2]$ (E = S, Se; R = ^{i}Pr, ^{t}Bu) with the cyclic cations $[N(PR_2Te)_2]^+I^-$ (R = ^{i}Pr, ^{t}Bu) (*vide infra)* proved to be an excellent route to such dimeric systems.[12] Surprisingly, this protocol led to two different CIP structures depending on the nature of the R groups attached to phosphorus. *Tert*-butyl substituents give rise to the spirocyclic CIPs **5b′** and **5c′**, whereas the corresponding *iso*-propyl derivatives **5b** and **5c** adopt a new CIP framework in which the five-membered acyclic anion $[N(P^iPr_2E)_2]^-$ (E = S, Se) is coordinated in an *E-monodentate* fashion to the cyclic cation $[N(P^iPr_2Te)_2]^+$.[12] DFT calculations indicate that the observed bidentate coordination mode is more stable than the monodentate isomer by 35-45 kJ mol^{-1} for the *tert*-butyl derivatives **5a′-c′,** but preferred by only 5-10 kJ mol^{-1} for the *iso*-propyl analogues **5b** and **5c;** crystal packing forces may be responsible for the observed formation of monodentate arrangement in the latter case.[12]

The trends in Te–Te bond lengths along the series **5a′** (2.981 Å), **5b′** (2.922 Å) and **5c′** (2.868 Å) indicate that the incipient cation in the CIP is more well-developed upon going from Te to S in the counter-anion. Comparison of the bond orders of the central chalcogen–chalcogen bonds reveals that this trend is determined by the strength of the anion–cation interaction. Thus, the Te–Te bond order increases as the E–Te bond order decreases.[12] Consistently, DFT calculations predict that the extent of electron transfer is 0.20 e^- for **5a′**, 0.39 e^- for **5b′,** and 0.50 e^- for **5c′**.[12]

3.2. Two-electron Oxidation. The facile formation of dimers upon one-electron oxidation of the monoanions $[N(PR_2E)_2]^-$ (E = S, Se, Te; R = ^{i}Pr, ^{t}Bu) evoked the possibility of generating the corresponding monocations via two-electron oxidation. Indeed, symmetrical cations of the type $[N(P^iPr_2E)_2]^+$ are readily generated as the surprisingly air-stable iodide salts **6a** and **6b** by oxidation of the corresponding anions with one equivalent of I_2 (Scheme 2).[13] The mixed chalcogen systems **6c** and **6d** are prepared in a similar manner.[11] The hexafluoroantimonate salts **7a**,**b** are produced by metathesis of the corresponding iodide salts with $Ag[SbF_6]$ (Scheme 2).[14]

The salts **6a** and **6b** are comprised of a five-membered cyclic cation $[N(P^iPr_2E)_2]^+$ and an iodide counterion that interacts with one of the chalcogens to form an infinite chain structure (Figure 2).[13] By contrast, the *tert*-butyl derivatives $[N(P^tBu_2E)_2]I$ (E = Se, Te) are dimeric with close Se–Se and Te–Te contacts, while the sulfur system $[N(P^tBu_2S)_2]I_3$ is an ion-separated monomer with a triiodide counterion.[9] In the mixed chalcogen systems **6c** and **6d** the iodide counterion interacts preferentially with the tellurium center.[11] The Te–I interaction is much stronger with the mixed chalcogen cations (**6c** and **6d**) than that in the ditellurido cation (**6a**) to the extent that the former are essentially monomeric in the solid state.

Simple electron-counting rules predict that the cyclic cations $[N(PR_2E)_2]^+$ are 6 π-electron systems. DFT calculations confirm this prediction, but reveal that the *net* π-bond order within the five-membered ring is close to zero. The three highest occupied orbitals are indeed π-type orbitals (Figure 3). However, the bonding effect of the E–E π–bonding orbital (HOMO−2) is essentially cancelled by the double occupation of the HOMO, which is the E–E π^*-antibonding orbital. The third occupied π-orbital (HOMO−1) is a primarily non-bonding nitrogen-centered orbital.

The stronger iodide–chalcogen interaction in the mixed chalcogen salts **6c** and **6d** produces a more pronounced elongation of the chalcogen–chalcogen bonds in the cyclic cations (**6c**, 8 %; **6d**, 12 %)[11] than that observed for the Te–Te bond in **6a** (4 %).[13a] The latter is attributed to the donation of electron density from a lone pair on the iodide counterion into the Te–Te σ^* orbital (LUMO) (Figure 3) of the symmetrical cation in **6a**,[13a,b] cf. the elongation of the I–I bond observed in the formation of the triiodide anion I_3^- from interaction of an I^- anion and an I–I molecule. The σ^* orbital (LUMO) in the mixed cations **6c** and **6d** is polarized towards tellurium (the more electropositive chalcogen) resulting in a stronger Te–I interaction and, concomitantly, a more pronounced lengthening of the E–Te bond.[11]

3.3 Solution NMR Studies. NMR spectra provide a wealth of information about the solution behavior of tellurium- and selenium-containing imidodiphosphinates as a result of the presence of spin-½ nuclei: ^{31}P (100 %), ^{77}Se (7.6 %) and ^{125}Te (7.0 %). The appearance of ^{77}Se and ^{125}Te satellites associated with ^{31}P resonances is a clear indicator of the P-E functionality, while the magnitude of the coupling constants ^{1}J(PSe) and ^{1}J(PTe) is inversely proportional to the P-E bond lengths and can be used to distinguish between terminal and bridging E atoms.[14a] Approximate ranges for ^{1}J(PSe) and ^{1}J(PTe) are 750-350 and 1750-850 Hz, respectively; terminal P=E bonds are identified by values at the high end of those ranges.[14a,b]

The NMR spectra of tellurium- or selenium-containing imidodiphosphinates have provided an initial indication of unexpected structures. For example, the ^{31}P NMR spectra on the monochalcogenides **1a** and **1b** showed one resonance with ^{1}J(PE) values consistent with terminal a P=E bond and a second resonance which revealed ^{1}J(PH) = 440-445 Hz, signifying the formation of the P-H tautomer.[6] The NMR spectra of the dimeric structures shown in Chart 1 are also revealing. At room temperature the ^{31}P NMR spectra of the dichalcogenides (DCs), e.g. **4a** (E = E′ = Te; R = ^{i}Pr) exhibit a broad, unresolved resonance indicative of a fluxional process. At low temperatures a pair of mutually coupled doublets is resolved with ^{1}J(PTe) = 1500 and 1026 Hz, consistent with the solid-state structure.[6] By contrast, the observation of *four* resonances in the low temperature ^{31}P NMR spectrum of the *tert*-butyl derivative **5a′** was a signal of a different structure, subsequently shown to be a contact ion pair (CIPs, Chart 1).[9]

^{31}P NMR spectra are also diagnostic of the purity of the Li derivatives of mixed chalcogen ligands, **2b** and **2c**, which exhibit characteristic satellite peaks, since the presence of the corresponding symmetrical ligands is readily detected.[10] In contrast to the behavior of the mixed selenotellurophosphinate $[Ph_2P(Se)Te][[Li(THF)_2(TMEDA)]$,[15] no chalcogen exchange was detected in the NMR spectra of **2b** and **2c**.[11] The formation of the Te-Te bonded isomer **4b** from oxidation of **2b** was clearly indicated by the observation of a terminal P=Se coupling of 639 Hz.[11]

4. Coordination Chemistry

4.1. **Complexes of $[N(P^iPr_2Te)_2]^-$.** Although the primary incentive for the preparation of homoleptic complexes of the anion $[N(P^iPr_2Te)_2]^-$ was the generation of new single-source precursors to metal tellurides, we found that this Te,Te′-chelating ligand exhibits significant differences in coordination behavior in comparison with the well-studied bonding patterns of the analogous disulfido and diselenido-imidodiphosphinate ligands.

Metathetical reactions between **2a** and a variety of main group, transition-metal, lanthanide and actinide halides produce homoleptic complexes $M[N(P^iPr_2Te)_2]_n$[16] with square planar (**8**, n = 2; M = Ni,[17] Pd,[18] Pt[18]), distorted tetrahedral (**9**, n = 2; M = Zn, Cd, Hg),[8] or distorted octahedral (**10**, n = 3; M = Sb,[8] Bi,[8] La,[19a] U,[19a] Pu,[19b] Ce[19b]) geometries. DFT calculations indicate a high degree of covalency for the U–Te bonds in the uranium(III) complex **10d**,[19b] the first example of a molecular compound with actinide–tellurium bonds. The square-planar structure of **8a** is maintained in solution, whereas the sulfur analogue adopts a tetrahedral geometry and the corresponding selenium complex has been isolated as both tetrahedral and square-planar stereoisomers in the solid state.[17] Homoleptic group 10 complexes of mixed chalcogen ligands $M[N(P^iPr_2Te)(P^iPr_2E)]_2$ (M = Ni. Pd, Pt; E = S, Se) are prepared by metathesis between the Li reagents **2b** or **2c** and $NiBr_2(DME)$[20] (DME = dimethoxyethane) or $MCl_2(COD)$ (M = Pd, Pt; COD = 1,5-cyclooctadiene).[18] The Ni(II) complexes are isolated as the square-planar *trans* isomers,[20] while the Pd and Pt complexes exist as a mixture of *cis* and *trans* isomers in solution.[18]

The homoleptic group 14 complexes $M[N(P^iPr_2Te)_2]_2$ (**11a**, M = Sn; **11b**, M = Pb) adopt *pseudo*-trigonal bipyramidal structures, reflecting the stereochemical influence of the lone pair on the metal center; weak intermolecular M···Te interactions result in dimeric arrangements.[21] The thallium(I) complex $\{Tl[N(TeP^iPr_2)_2]\}_\infty$, which is prepared from **2a** and TlOEt, is the first example of a molecular complex containing Tl–Te bonds. It is comprised of infinite chains linked by Tl···Te interactions in which six-coordinate Tl centers are bridged by two different $[N(P^iPr_2Te)_2]^-$ ligands arranged approximately perpendicular to each other.[22] The selenium analogue $\{Tl[N(SeP^iPr_2)_2]\}_\infty$ has a similar polymeric structure with both 5- and 6-coordinate Tl centers, whereas the sulfur congener $\{Tl[N(SP^iPr_2)_2]\}_\infty$ is a ladder-like polymer with 4-coordinate Tl centers, cf. $\{K[N(SPPh_2)_2]\}_\infty$.[23]

Coinage metal complexes of the ditellurido anion $[N(P^iPr_2E)_2]^-$ (E = Te) exhibit interesting structural differences when compared to the analogous complexes of the disulfido (E = S) and diselenido (E = Se) ligands as a result of the propensity of the ditellurido ligand to adopt a doubly bridging bonding mode.[24] One of the ligands in the trimeric copper(I) complex $\{Cu[N(P^iPr_2Te)_2]\}_3$ (**12**) exhibits this behavior resulting in two short (ca. 2.63 Å) and one long (ca. 3.58 Å) Cu-Cu distance, whereas the analogous disulfido and diselenido ligands in $\{Cu[N(P^iPr_2E)_2]\}_3$ (**13a,b**) all behave as singly bridging ligands and the three Cu atoms form an equilateral triangle.[25, 26] The greater flexibility of the ditellurido ligand $[N(P^iPr_2Te)_2]^-$ is also evident in the silver(I) complex $\{Ag[N(P^iPr_2Te)_2]\}_6$ (**14a**), which forms a hexamer comprised of a twelve-membered Ag_6Te_6 ring,[24] whereas the selenium analogue is trimeric $\{Ag[N(P^iPr_2Se)_2]\}_3$, cf. **13a**.[25] A change of the substituents on phosphorus from *iso*-propyl to phenyl in the ditellurido ligand gives rise to a profound structural change. The complex $\{Ag[N(PPh_2Te)_2]\}_4$ **(14b)** adopts a tetrameric structure in the form of a centrosymmetric, chair-shaped eight-membered Ag_4Te_4 ring.[24] The doubly bridging mode of one of the $[N(PPh_2Te)_2]^-$ ligands in the tetramer creates a 4-coordinate environment for one of the Ag atoms and short transannular Ag···Ag contacts between the 3-coordinate Ag centers. The distortion of the latter from trigonal planar geometry ($\Sigma{<}Ag = 345^\circ$) may indicate a metallophilic interaction.

4.2. Complexes of $[TeP^iPr_2N^iPr_2P]^-$. Although it is thermally unstable (due to disproportionation), we have demonstrated that the lithium reagent $Li[TeP^iPr_2N^iPr_2P]$ (**3a**) can be generated by lithiation of **1a** at −78 °C (Scheme 1) and, subsequently, used for *in situ* metathesis with metal halides. In this way homoleptic complexes of the type $M(TeP^iPr_2N^iPr_2P)_2$ with distorted tetrahedral (M = Zn, Cd, Hg)[27] or square-planar (M = Ni,[20] Pd,[18] Pt[18]) structures are obtained via metathesis. The Ni complex is formed exclusively as the *trans* isomer whereas the Pd analogue exists as a mixture of the isomers *cis*-**16a** and *trans*-**16a,**[18] which can be separated by fractional crystallization. In the case of Pt the major product from the reaction with $PtCl_2(COD)$ is the unusual complex $Pt[(P^iPr_2)(TeP^iPr_2)N][\sigma:\eta^2\text{-}C_8H_{12}(P^iPr_2NP^iPr_2Te)]$ (**17**) resulting from nucleophilic attack of the phosphorus(III)-centered anion $[TeP^iPr_2N^iPr_2P]^-$ on the coordinated COD ligand; *trans*-**16b** is the minor product of this reaction.[18]

The group 11 complexes $\{M(TeP^iPr_2N^iPr_2P)\}_3$ (**15a**, M = Cu; **15b**, M = Ag) have particularly interesting trimeric frameworks in which the tellurium centers bridge two metal atoms to give highly distorted chair-like M_3Te_3 rings with short M–M distances.[28] During the X-ray structural investigations of **15a,** we observed that air oxidation of the yellow crystals in Paratone oil gave a few colorless crystals of the mixed chalcogen complex $\{Cu(TeP^iPr_2N^iPr_2PO)\}_3$.[28] This fascinating transformation (oxygen insertion into a Cu–P bond) inspired us to investigate the reactions of the labile trimer **15a** with chalcogens.[28] By choosing appropriate conditions, we found that the series of mixed chalcogen complexes$\{Cu(TeP^iPr_2N^iPr_2PE)\}_3$ (**18a**, E = O; **18b**, E = S; **18c**, E = Se) are formed upon treatment of **15a** with Me_3NO, elemental sulfur or red selenium, respectively (eq. 3).[28] The complex **18a** features the first example of a Te,O-centered ligand of this type. The complexes **18a-c** all exhibit a trinuclear structure with the tellurium centers occupying the bridging positions to give a chair-like Cu_3Te_3 ring in which the trigonal planar copper centers form an approximately equilateral triangle.

4.3. Intramolecular Oxidative Additions. We observed another manifestation of the unique behavior of the ditellurido ligands $[N(PR_2Te)_2]^-$ in the attempted synthesis of homoleptic complexes of gallium(III),[29] indium(III),[29]and gold(I);[30] for all three metals a tellurium-transfer process occurs to give novel metal–tellurium rings. Thus the reaction of **2a** with gallium trichloride produced the dimeric Ga^{III} complex $\{Ga(\mu\text{-}Te)[{}^{i}Pr_2PN{}^{i}Pr_2PTe]\}_2$ (**19**) and the ditelluride dimer **4a.** A possible pathway for the formation of **19** involves reductive elimination of **4a** from the homoleptic Ga^{III} complex $Ga[N(P{}^{i}Pr_2Te)_2]_3$ (**20**) to give the Ga^{I} complex $Ga[N(P{}^{i}Pr_2Te)_2]$ (**21**), which undergoes tellurium transfer (intramolecular oxidative addition) to give the Ga_2Te_2 dimer **19** via the unstable gallatellurone **22** (Scheme 3). Both *cis* and *trans* isomers of **19** are present in solutions, but the *trans* isomer crystallizes preferentially.[29]

We also discerned intramolecular oxidative addition in the attempted metathesis of **2a** with indium trichloride, which produced a low yield of the trimeric complex $\{In(\mu\text{-}Te)[N({}^{i}Pr_2PTe)_2]\}_3$ (**23a**) comprised of a central In_3Te_3 ring.[29] Subsequently, we devised a high-yield synthesis of this novel In^{III} complex involving the metathesis of In(I)Cl with **2a** *in the presence of* elemental tellurium (eq. 2). The gallium analogue **23b** is obtained in a similar manner by using GaI instead of InCl.[29]

The strongly reducing nature of the ditellurido anions $[N(PR_2Te)_2]^-$ is evident in the reaction of **2a** with gold(I) chloride, which rapidly produces a gold mirror.[24] We found that this process can be prevented by the addition of a two-electron donor prior to the metathesis. Thus, the reaction of **2a** with AuCl *in the presence of* triphenylphosphine, produces the monomeric complex $Au(PPh_3)[N(P{}^{i}Pr_2Te)_2]$ (**24**).[24] Intriguingly, the use of (THT)AuCl (THT = tetrahydrothiophene) as the source of gold(I) results in the formation of the dimeric gold(III) complexes $\{Au(\mu\text{-}Te)[R_2PNR_2PTe]\}_2$ (**25**)[30] as a mixture of *cis* and *trans* isomers; the *trans* isomer crystallizes preferentially. The formation of the central Au_2Te_2 ring formally involves an intramolecular oxidative addition reminiscent of that proposed for the generation of the Ga_2Te_2 ring (Scheme 3). Interestingly, in the case of the Au–Te system, this process is reversible upon addition of PPh_3 to give the monomeric gold(I) complex **24** (eq. 3).[30]

4.4 Solution NMR Studies. ^{31}P NMR studies of coordination complexes of ditelluroimidodiphosphinates have revealed the presence of isomeric or oligomeric species in solution. For example, *cis* and *trans* isomers are apparent for the Ga complex **19** (Scheme 3)[29] and the Au complexes **25** (Eq. 3).[30] In the latter case the determination of the solid-state ^{31}P NMR spectrum of **25** (R = ^{i}Pr) facilitated the assignment of the resonances in the solution spectrum to the individual isomers.[30] NMR spectra also provide decisive structural information for the series of Ni(II) complexes $Ni[N(P^{i}Pr_2E)_2]_2$ (E = S, Se, Te) in solution.[17] Although the Se analogue exists as either a square-planar (diamagnetic) or a tetrahedral (paramagnetic) complex in the solid state, both isomers exhibit a paramagnetically shifted ^{31}P NMR resonance indicating only the T_d isomer prevails in solution; the S and Te analogues maintain their tetrahedral and square-planar structures, respectively.[17] Additionally, the low-temperature ^{31}P NMR spectra of d_8-THF solutions of the Cu(II) and Ag(I) complexes **15a,b** yielded evidence that these species, which are trimeric in the solid state, form a mixture of oligomers which are in dynamic equilibrium.[28]

5. Single-Source Precursors for Metal Tellurides

Current interest in metal tellurides, e.g. CdTe, Sb_2Te_3, PbTe, emanates from their potential uses as low-band-gap semiconducting materials in solar cells, thermoelectric devices, and telecommunications. Metal complexes of a number of tellurium-centered ligands have been investigated as single-source precursors of binary metal tellurides. These include the group 14 tellurolates $M[Te\{Si(SiMe_3)_3\}]_2$ (M = Sn, Pb),[31] the *N*,*Te*-chelated complexes $M[NR(Te)P^tBu_2]_2$ (M = Zn, Cd; R = ^{i}Pr, Cy),[32] and the six-membered ring $(Bn_2SnTe)_3$ (Bn = benzyl).[33] In all these examples thermolysis produced thin films of metal tellurides that were contaminated with small amounts of carbon and/or the metal. More recently, an isopropylgermanium tellurolate has been used to generate GeTe thin films by using CVD techniques.[34] An evaluation of the suitability of the homoleptic ditelluridoimidodiphosphinate complexes of group 11, 12, 14 and 15, as well as the group 13 complexes **23a**,**b,** as single-source precursors for metal tellurides using the AACVD technique has been carried out in collaboration with O'Brien and co-workers.[35] The results are summarized in Table 1, which shows that this method is successful for producing pure thin films of CdTe,[36] Sb_2Te_3,[37] In_2Te_3,[38] and PbTe[21] under appropriate conditions. For some precursors, however, AACVD produces only elemental tellurium (**9c, 10b, 11a)** or a mixture of a metal telluride and tellurium (**12, 23b, 24**). The formation of elemental tellurium in some cases is perhaps not unexpected in view of the high Te:M ratio in the precursors, however the use of a homoleptic mercury complex of the *mono*tellurido ligand $[TeP^iPr_2N^iPr_2P]^-$ did not produce pure HgTe.

Attempts to produce ternary nickel chalcogenides from the mixed chalcogen complexes $Ni[N(^iPr_2PSe)(^iPr_2PE)]_2$ generated the binary chalcogenide $NiTe_2$ by AACVD when E = Te[20] or both nickel phosphide (Ni_2P) and nickel selenide ($Ni_{0.85}Se$) by LPCVD for E = S.[39] The reason for the preferential formation of the heavier chalcogenide from these SSPs has not been established.

6. Conclusions

In summary, comprehensive investigations of the redox behavior and coordination complexes of anionic tellurium-centered imidodiphosphinates have provided new insights into the chemistry of this well-established class of inorganic ligand. One-electron oxidation provides a variety of dimers whose structures are influenced by the nature of the chalcogen as well as the organic substituent on phosphorus; two-electron oxidation generates novel cyclic cations. In conjunction with DFT calculations, the structural data for these dimers and cations have enhanced our understanding of chalcogen-chalcogen bonding. Significant differences in the coordination behavior of the tellurium-centered ligands compared to that of their lighter chalcogen analogues was observed as a result of (a) the larger size of tellurium and (b) the weakness of P–Te bonds. The former is manifested in the tendency for the tellurium ligands to adopt a doubly bridging coordination mode leading to unprecedented structures and, in the case of coinage metals, the possibility of metallophilic interactions. The lability of P–Te bonds is demonstrated by the occurrence of tellurium-transfer processes (intramolecular oxidative additions) that generate novel metal–tellurium rings. It is also evident in the use of metal complexes as single-source precursors to thin films of binary metal tellurides. The majority of our work has been carried out on ligands with isopropyl (or tert-butyl) substitutents on phosphorus. However, preliminary investigations presage that significantly different chemistry will be observed for the phenyl-substituted analogues.[13b]

All of this work was funded by NSERC (Canada). Pivotal contributions to the early investigations by Drs Glen G. Briand, Dana J. Eisler and May C. Copsey and the collaboration with Prof. P. O'Brien and Dr M. Afzaal (University of Manchester, UK) *on the generation of metal tellurides from single-source precursors are gratefully acknowledged.*

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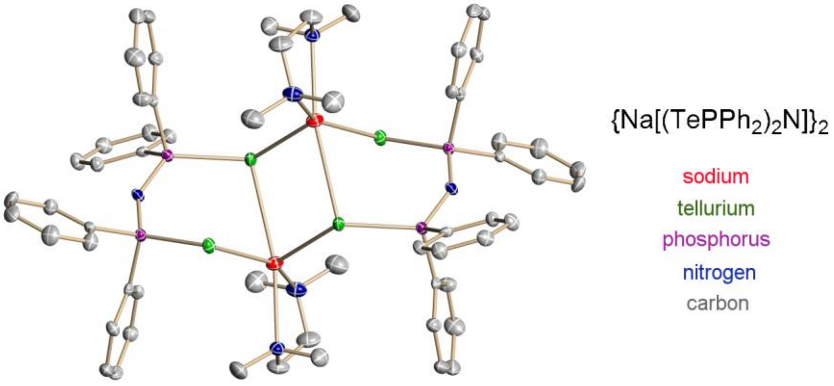
Table 1. Formation of Metal Tellurides from Single-Source (SS) Precursors

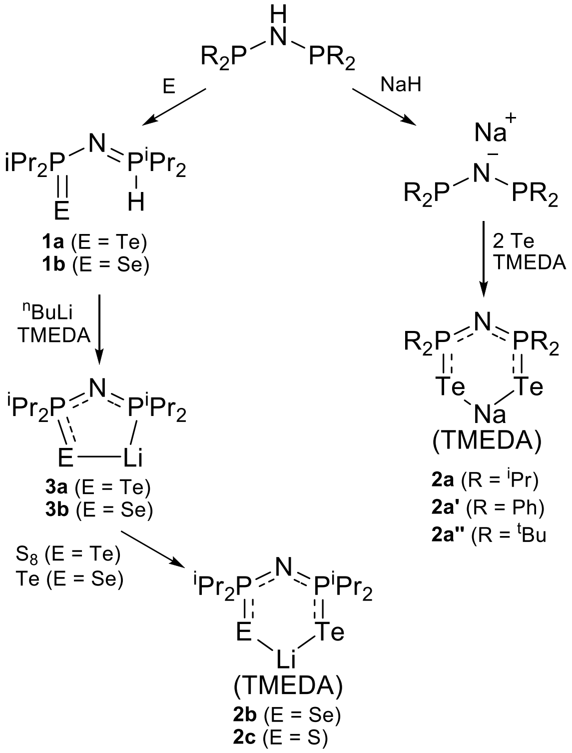
Precursor	Products	Ref.
9b	Cubic CdTe	36
9c	Hexagonal Te	36
10a	Rhombohedral Sb_2Te_3	37
11b	PbTe	21
12	Orthorhombic CuTe + Te	23
14a	Ag_7Te_4 + Te	23
23a	Cubic In_2Te_3	38
23b	Cubic Ga_2Te_3, GaTe + Te	38
24	Monoclinic $AuTe_2$ + Te	23
a	Hexagonal $NiTe_2$	20

a $Ni[N(^{i}Pr_2PSe)(^{i}Pr_2PTe)]$

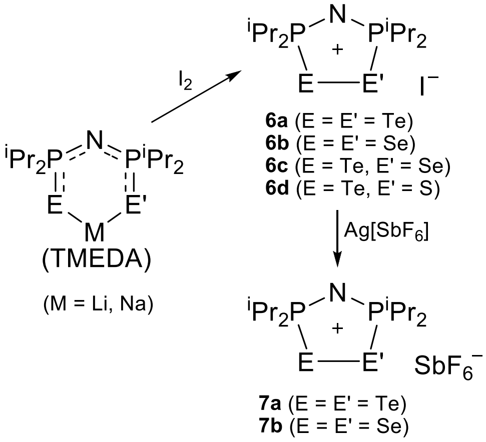
Conspectus image.



Scheme 1.



Scheme 2.



Scheme 3

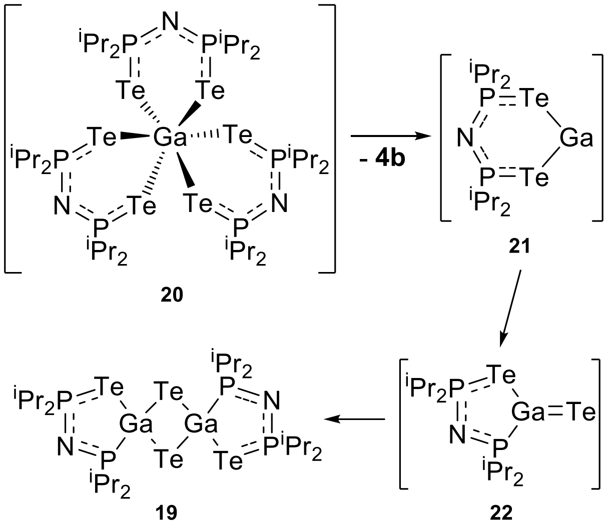


Chart 1.

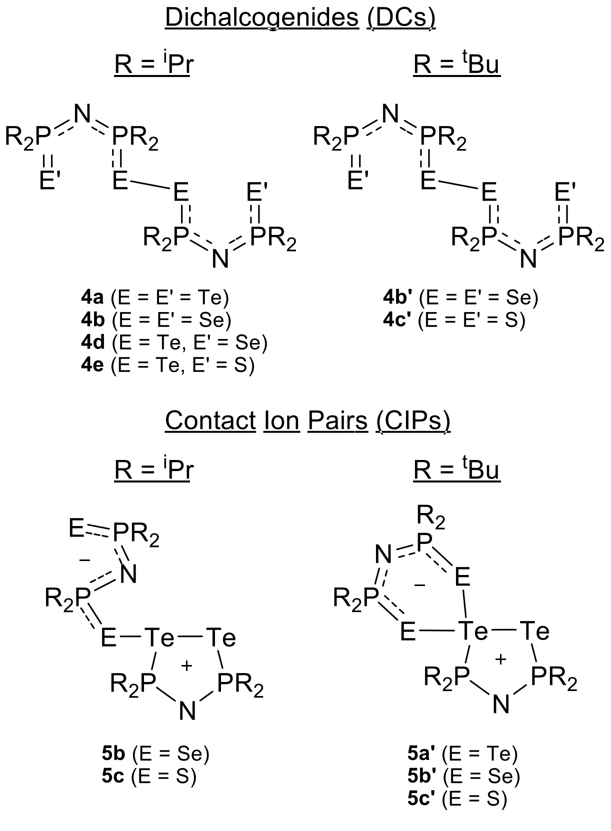
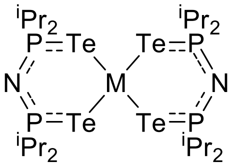
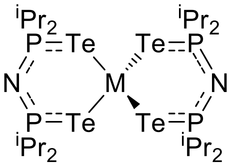


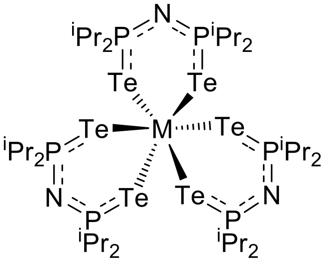
Chart 2



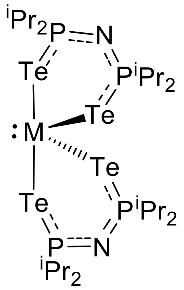
8a (M = Ni)
8b (M = Pd)
8c (M = Pt)



9a (M = Zn)
9b (M = Cd)
9c (M = Hg)

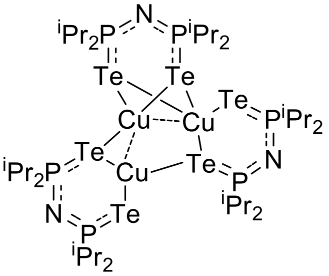


10a (M = Sb) **10c** (M = La)
10b (M = Bi) **10d** (M = U)
10e (M = Pu)

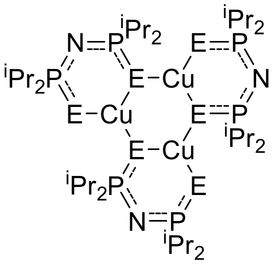


11a (M = Sn)
11b (M = Pb)

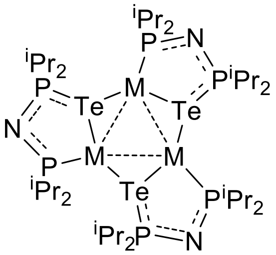
Chart 3



12

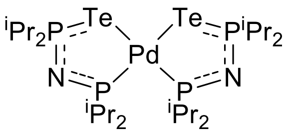


13a (E = Se)
13b (E = S)

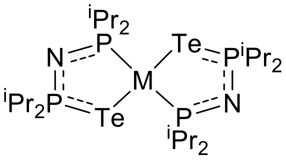


15a (M = Cu)
15b (M = Ag)

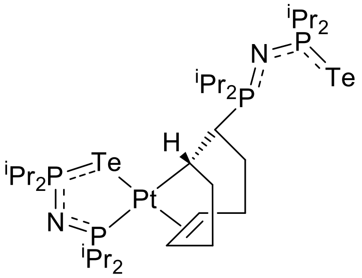
Chart 4



cis-**16a**



trans-**16a** (M = Pd)
trans-**16b** (M = Pt)



17

Figure 1

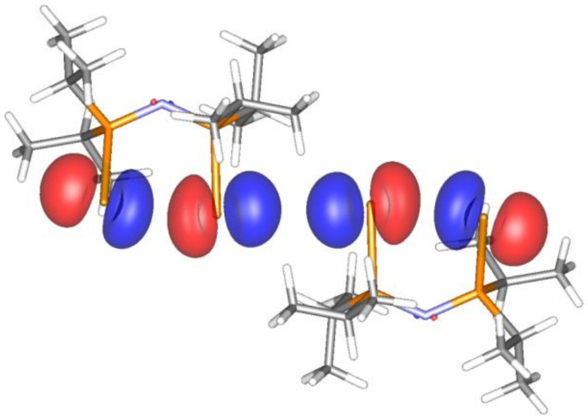


Figure 2

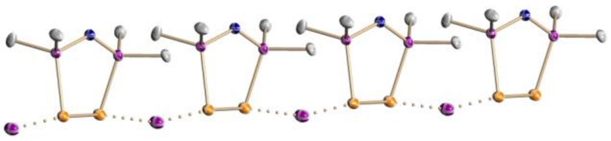
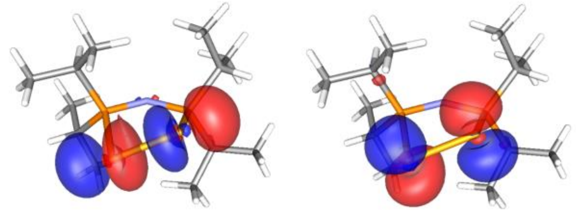
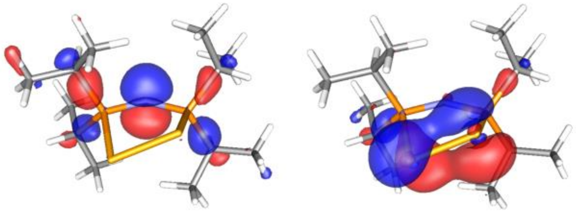


Figure 3

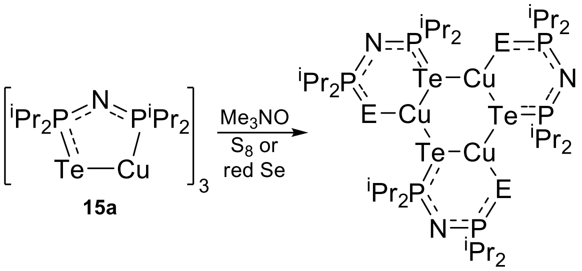


LUMO HOMO



HOMO-1 HOMO-2

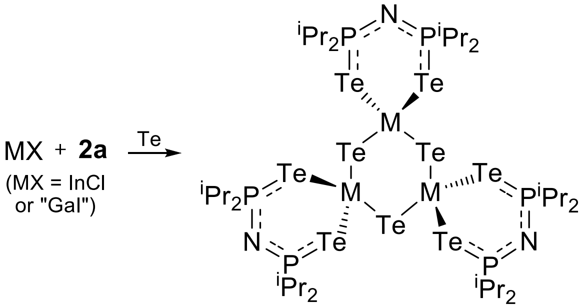
Equations



15a

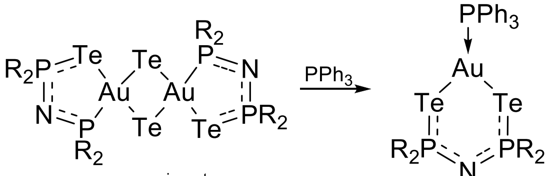
16a (E = O)
16b (E = S)
16c (E = Se)

(1)



23a (M = In)
23b (M = Ga)

(2)



25 (R = Ph, ^{i}Pr, ^{t}Bu)

24

(3)

List of Figure and Scheme Captions

SCHEME 1. Synthesis of mono and dichalcogenido imidodiphosphinate ligands

SCHEME 2. Synthesis of cyclic cations $[N(P^{i}Pr_2E)_2]^+$ (E = Se, Te)

SCHEME 3. Formation of a Ga_2Te_2 ring via intramolecular oxidative addition

FIGURE 1. Bonding interaction between two $[TeP^{i}Pr_2N^{i}Pr_2PTe]^{\bullet}$ SOMOs

FIGURE 2. Polymeric structure of $[N(P^{i}Pr_2E)_2]I$ (E = Se, Te). Methyl groups and hydrogen atoms are omitted for clarity.

FIGURE 3. Frontier MOs of the cations $[N(P^{i}Pr_2E)_2]^+$ (E = Se, Te)