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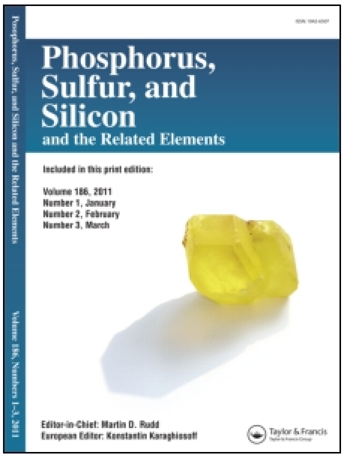

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Recent Studies of Multiply Bonded Selenium and Tellurium Compounds

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Several aspects of recent developments in the chemistry of multiply bonded selenium and tellurium compounds are surveyed in this article. These include (a) tellurium(IV)-nitrogen compounds, (b) complexes with two (or more) terminal Group 14–Group 16 linkages, and (c) a new approach to previously inaccessible ligands containing Group 15–Group 16 functionalities.

Keywords Group 14; Group 15; multiple bonds; nitrogen; selenium; tellurium

INTRODUCTION

Compounds involving multiple bonds between selenium or tellurium and p-block elements are often unstable with respect to either singly bonded alternatives or the formation of the elemental chalcogen.[1] In addition to the fundamental interest in the structure, bonding, and reactivity of such compounds, they are of potential interest in the construction of single-source precursors to binary chalcogenide semiconductors. This article will survey recent developments in three aspects of the chemistry of multiply bonded selenium and tellurium compounds.

TELLURIUM(IV)—NITROGEN COMPOUNDS

The unexpected formation and X-ray structural characterization of the first tellurium(IV) diimide was first reported in 1994.[2] Shortly after this discovery we developed a synthesis of the symmetrical tellurium diimide dimer **1** from the reaction of tellurium tetrachloride with $LiNH^tBu$ in toluene at −80°C.[3] The yields of **1** are substantially

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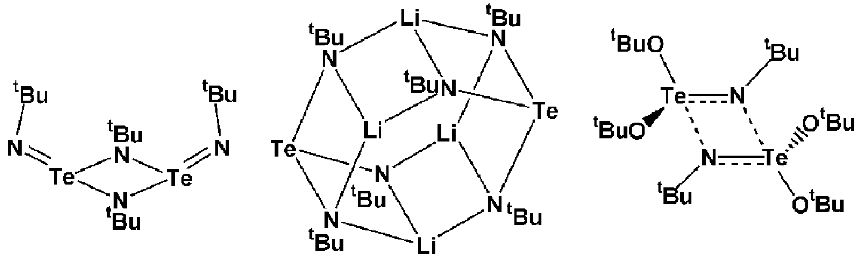
improved (*ca.* 90%) when this reaction is carried out in tebahydrofuran (THF).[4] The early developments in the chemistry of **1**, including the reaction with $LiNH^tBu$ to produce $\{Li_2[Te(N^tBu)_3]\}$ (**2**),[5] (Scheme 1) were presented at the ICCST-7 meeting in Aachen, Germany in 1997.[6]



1 2 3

SCHEME 1

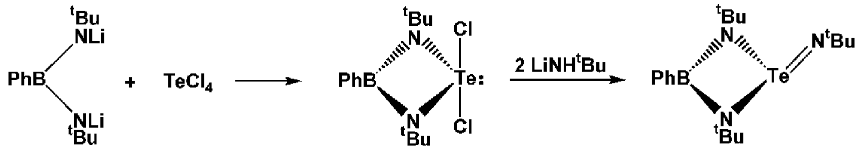
Significant new findings that have been reported more recently include the preparation and structural characterization of (a) the imidotellurium(IV) dihalides $(^tBuNTeX_2)_n$ (X = Cl, Br),[7] (b) the imidotelloroxane $(^tBuNTeO)_4$ as an adduct with $B(C_6F_5)_3$,[8] (c) the cycloaddition reactions of **1** with heteroallenes, e.g. ^tBuNCO,[9] and (d) coordination complexes of **1** with coinage metals.[10]

The reaction of **1** with tellurium tetrahalides in THF gives high yields of $(^tBuNTeX_2)_n$ (X = Cl, Br) (Eq. (1)). The dichloride forms mica-like crystals, which were shown to have a hexameric structure formed by linking three $(^tBuNTeCl_2)_2$ dimers via chloride bridges.[7] The layers of hexameric units are further linked by weak Te$\cdots$Cl contacts.

$$^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu + 2TeX_4 \mapsto (4/n)[^tBuNTeX_2]_n \qquad (1)$$

The imidotellurium(IV) dihalides are useful reagents for the development of Te-N chemistry via metathetical reactions. For example, the reaction of $(^tBuNTeCl_2)_n$ with two equivalents of potassium *tert*-butoxide produces the dimer $(^tBuO)_2Te(\mu\text{-}N^tBu)_2Te(O^tBu)_2$ (**3**) in which the central Te_2N_2 ring is markedly asymmetric [d(Te—N) = 1.94 and 2.22 Å], suggesting that a monomeric tellurium imide $(RO)_2Te{=}N^tBu$ might be generated if sufficiently bulky alkoxy or aryloxy groups are attached to tellurium. The monomeric tellurium imide $PhB(\mu\text{-}N^tBu)_2Te{=}N^tBu$ (**4**), which was previously obtained from the reaction of **2** with $PhBCl_2$,[5] has now been prepared by an alternative pathway (Scheme 2).[11]

The synthesis of hybrid imido-oxo tellurium(IV) compounds, e.g. $(^tBuNTeO)_n$, represents a challenge because the hydrolysis of **1** produces $(TeO_2)_\infty$ even when a deficiency of water is used. However, we



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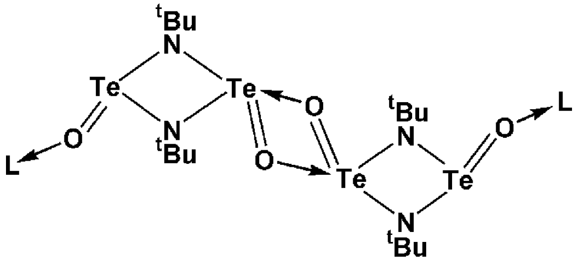
SCHEME 2 Formation of a monomeric tellurium(IV) imide.

recently have been able to control the hydrolysis by using the hydrate $H_2O \cdot B(C_6F_5)_3$ as a stoichiometric reagent for the conversion of Te=N^{t}Bu into Te=O functionalities. The reaction of **1** with this reagent produces the di-adduct **5**.[8] The tetrameric association of the hybrid ^{t}BuNTeO species in **5** suggests that the removal of the two terminal $B(C_6F_5)_3$ ligands with a suitable Lewis base would generate the polymer $(^tBuNTeO)_\infty$ with alternating Te_2N_2 and Te_2O_2 rings (Scheme 3).

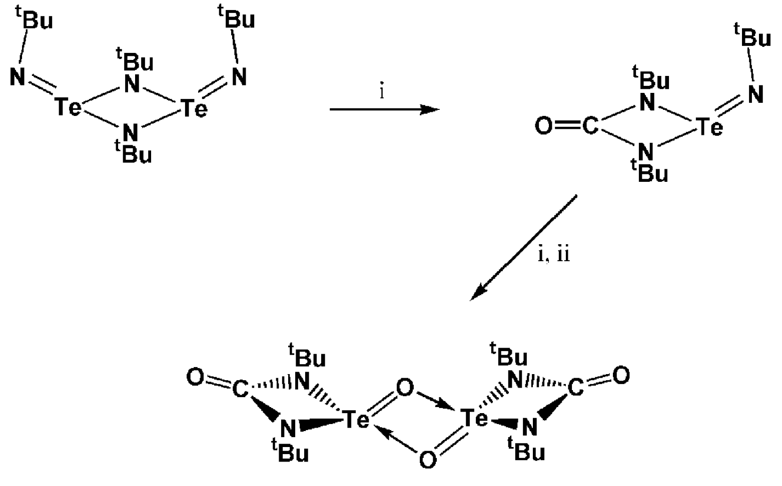


5 [L = $B(C_6F_5)_3$]

SCHEME 3

The tellurium diimide dimer **1** reacts readily with heteroallenes, e.g. CO_2, CS_2 or RNCO. In the case of ^{t}BuNCO, the reaction follows the pathway depicted in Scheme 4 to give the dimeric ureato telluroxide **6** in which the ureato ligands adopt a *cis* arrangement.[9] Complex **6** has an intriguing solid-state structure in which weak Te···O=C contacts between the dimeric units give rise to a polymeric helical network.

The dimer **1** is obtained as the *cis,endo,endo* isomer with respect to the orientation of the terminal N^{t}Bu groups.[3] A *trans,exo,exo* isomer has also been isolated,[2] but it undergoes isomerization to a cis isomer in organic solvents over the course of 1 day.[12] This structural flexibility suggests that **1** will be a versatile ligand acting in either a chelating or a bridging mode in coordination complexes. This versatility is exemplified in complexes of **1** with coinage metals.[10] In particular, Cu^+ promotes



6

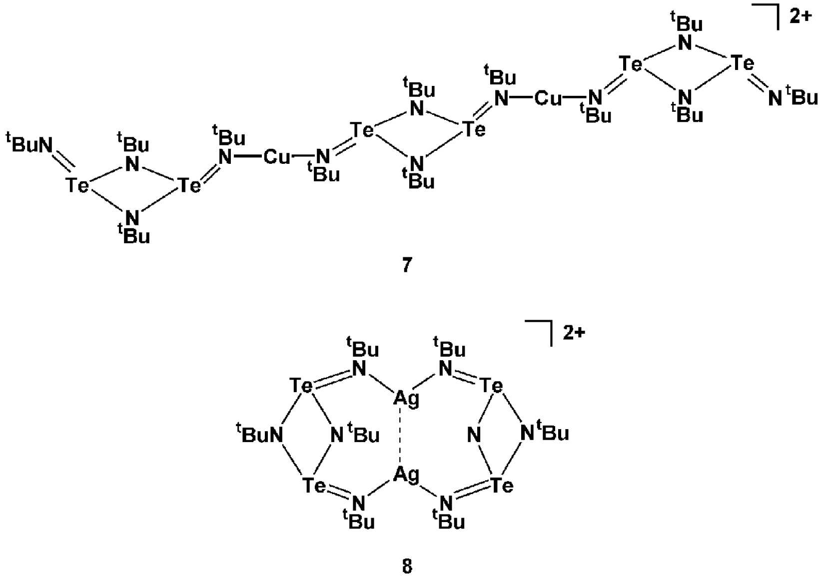
SCHEME 4 Reagents: (i) $+2^{t}BuNCO$ (ii) $-2^{t}BuNCN^{t}Bu$.

cis → *trans* isomerization of the ligand **1** to give the dinuclear complex **7** (Scheme 5) in which the central bridging ligand is in the *trans,exo,exo* configuration, while the terminal ligands retain the *cis* geometry but adopt an *endo,exo* arrangement of the terminal $N^{t}Bu$ groups. By contrast, the two Ag^{+} ions in the dinuclear silver complex **8** bridge two molecules of the ligand **1**, which are in the *cis,exo,exo* configuration. The nonlinearity of the N—Ag—N bond angle (163.3°) in **8** indicates the presence of a d^{10}-d^{10} metallophilic attraction.

The pyramidal trisimidotellurite $[Te(N^{t}Bu)_3]^{2-}$ in **2** is also a potentially versatile multidentate ligand. For example, it behaves as an *N,N′*-bidentate ligand in the boron complex **4**, but as a tridentate ligand in the binuclear indium complex **9** (Scheme 6).[13] The reactions of **2** with main group element halides may also result in redox behaviour. A dramatic example of the unexpected outcome of such transformations is the formation of the stannatellone **10** upon reaction of **2** with tin(II) salts.[14] Although a stannatellone containing five-coordinate tin was reported previously,[15] complex **10** is the first example of a Sn=Te double bond involving four-coordinate tin.

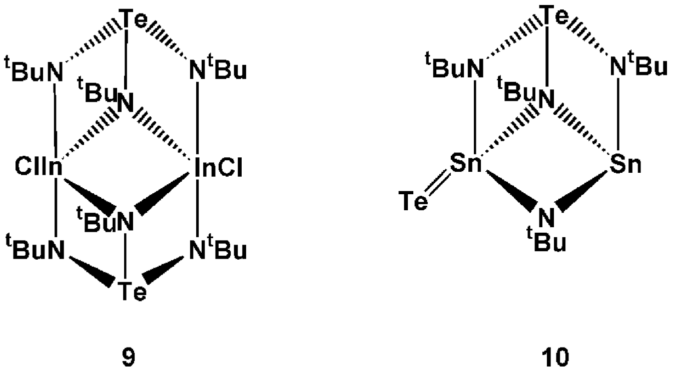
COMPLEXES WITH TWO (OR MORE) GROUP 14–GROUP 16 TERMINAL BONDS

There have been impressive advances in the range and diversity of compounds containing Group 14–Group 16 double bonds, also called *heavy*



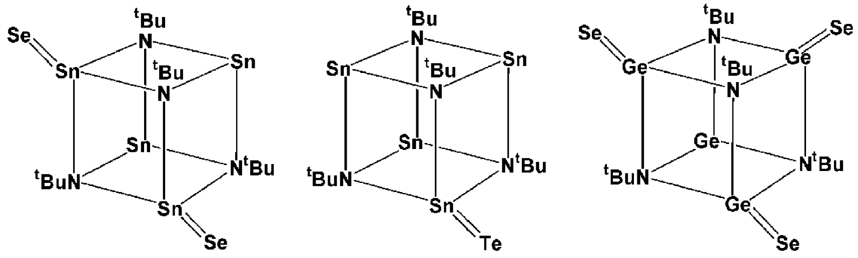
SCHEME 5

ketones, in the last 10 years.[16] These highly reactive functionalities may be stabilized either by attaching very bulky groups to the Group 14 element to give a genuine three-coordinate ketone analogue or by intramolecular heteroatom coordination to give four- or five-coordinate metal centers. The rare Sn=Te functionality in **10** is evidently stabilized by the three N^{t}Bu ligands attached to the tin center. This finding prompted us to investigate whether the oxidation of the well-known cubic system (SnN^{t}Bu)$_4$ by chalcogens provides a source of compounds containing more than one terminal Sn=E bonds (E = Se, Te).



SCHEME 6

The reaction of $(SnN^tBu)_4$ with an excess of elemental selenium in boiling toluene yields the distannaselone $Sn_4Se_2(N^tBu)_4$ (**11**), whereas the reaction with tellurium under similar conditions produces the monostannatellone $Sn_4Te(N^tBu)_4$ (**12**).[17] The Sn=E bond lengths in the complexes **10–12** fall within the expected range for Group 14–Group 16 double bonds involving four-coordinate tin. Apparently the oxidation of the remaining tin centers by chalcogens becomes more difficult after the initial oxidation of one or two of the Sn(II) sites in $(SnN^tBu)_4$. Consequently, we also investigated the oxidation of the germanium analogue $(GeN^tBu)_4$ with chalcogens with the expectation that the germanium(II) centers would be more easily oxidized than tin(II). Indeed the reaction of $(GeN^tBu)_4$ with an excess of selenium in boiling toluene yields the trigermaselone $Ge_4Se_3(NtBu)_4$(**13**).[17] The corresponding reaction with tellurium, however, produces the monogermatellone $Ge_4Te(N^tBu)_4$. Complexes **11** and **13** are the first examples of compounds containing more than one Group 14–Group 16 multiple bond.



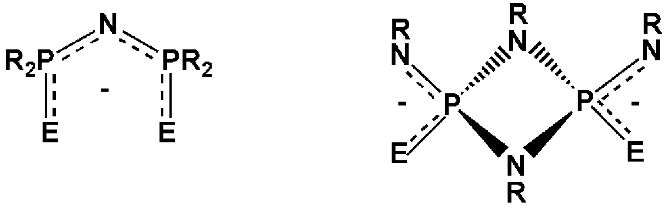
11 **12** **13**

SCHEME 7

A NEW APPROACH TO LIGANDS WITH MULTIPLY BONDED GROUP 15–GROUP 16 LINKAGES

Although monoanionic ligands of the type $[R_2P(E)NP(E)R_2]^-$ (**14**)[18] and dianionic ligands of the type $[RN(E)P(\mu\text{-}NR)_2P(E)NR]^{2-}$ (**15**)[19] (Scheme 8) have been extensively investigated, the tellurium analogues were, until recently, unknown. Attempts to make the neutral precursors for **14** and **15** (E = Te) were either unsuccessful or produced very low yields. Consequently, we adopted a different approach to these anionic ligands, which involves metalation of the neutral imido or amido phosphorus (III) compounds prior to oxidation with tellurium.[20]

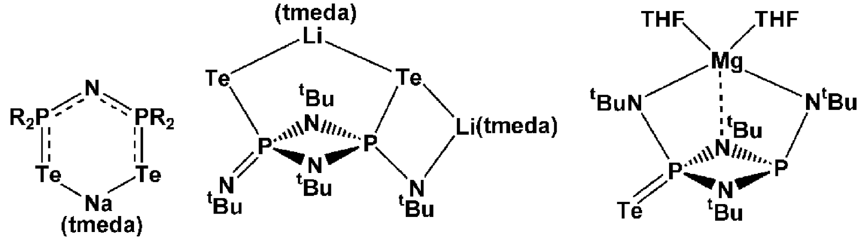
The reaction of $Na[Ph_2PNPPh_2]$ with tellurium powder in toluene at 80°C in the presence of tetramethylethylenediamine (TMEDA)



14 (E = O, S, Se) **15** (E = S, Se)

SCHEME 8

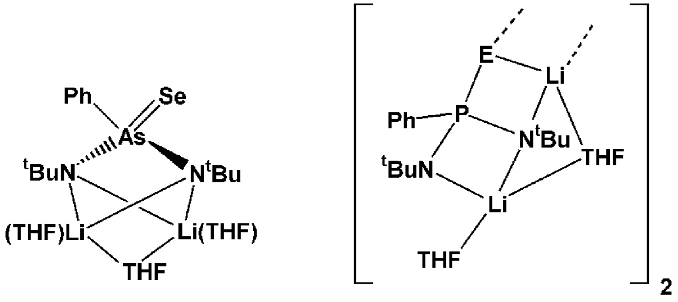
produces complex **16**, which adopts a dimeric structure with a central Na_2Te_2 ring in the solid state. The treatment of $[Li(thf)]_2[^tBuNP(\mu\text{-}N^tBu)_2PN^tBu]$ with tellurium under similar conditions yields complex **17**. The molecular structure of **17** (Scheme 9) reveals a unique bonding mode for ligands of the type **15** in which one Li^+ ion is coordinated in a *Te,Te′* fashion, while the second Li^+ ion is *N,Te* chelated by the dianion. A similar reaction involving the magnesium salt $[Mg(thf)]_2[^tBuNP(\mu\text{-}N^tBu)_2PN^tBu]$ yields the monotelluride **18**.[21] The sulfur analogue of **17** exhibits bis-*N,S* chelation to two Li^+ centers.[22] Attempts to make the selenium analogue of **17** by using deprotonation methodology led to cleavage of one of the P=Se bonds.[22]



16 **17** **18**

SCHEME 9

This new synthetic approach can be applied to the synthesis of related ligands containing Group 15–Group 16 functionalities. For example, the reaction of $Li_2[PhAs(N^tBu)_2]$ with selenium in THF at room temperature proceeds rapidly to give **19** (Scheme 10), a rare example of a complex containing a terminal As=Se bond.[23] The neutral compound $PhAs(NH^tBu)_2$ does not attributably react to THF solvation that effects four-coordination for both Li^+ centers. By contrast, the analogous phosphine selenide and telluride complexes, **20a** and **20b**, respectively,



19

20a (E = Se)
20b (E = Te)

SCHEME 10

adopt centrosymmetric dimeric structures with a central Li_2E_2 ring.[24] The telluride **20b** is prepared by the reaction of $Li_2[PhP(N^tBu)_2]$ with tellurium at 70°C in THF.[24]

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