Structural Studies of Lithium Telluro- and Seleno-Phosphorus Compounds

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Dedicated to the memory of Ron Snaith

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Lithium tellurophosphinite $[Ph_2PTe][Li(TMEDA)_{1.33}(THF)_{1.33}]$ (**4**), ditellurophosphinate, $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (**5**), and selenotellurophosphinate $[Ph_2P(Se)Te][Li(THF)_2(TMEDA)]$ (**6**) complexes have been prepared from the insertion/oxidation reactions of lithiated secondary phosphanes with elemental chalcogens and characterised by X-ray crystallography. Compounds **4**–**6** contain no tellurium–lithium bonding interactions in the solid state, instead existing as ion-separated species with THF/TMEDA-solvated lithium cations. Reaction of dilithiated primary phosphanes with more than three equivalents of elemental selenium gives $[\{(c\text{-}C_6H_{11})P(Se)(SeLi)\}_2\cdot 2TMEDA]$ (**7**) via a phosphorus-phosphorus coupling reaction. Solid state characterisation of **7** reveals the organo groups in the tetradentate tetraselenohypodisphosphinate ligand to be in an anti conformation to one another and each lithium atom to be coordinated by two selenium atoms, one from each of the diselenophosphinate groups. Multinuclear NMR spectroscopic data are consistent with retention of the solid-state structures of **4**–**7** in solution.

Introduction

Thiophosphorus ligands, in particular dithiophosphates and -phosphinates, have been reported extensively in the literature[1] and have found many applications including as lubricant oil additives[1,2] and as extraction agents for separation procedures.[3] In addition they have been shown to exhibit a broad variety of coordination patterns leading to a wide range of molecular and supramolecular structures.[1] However, the chemistry of the heavier group 16 homologues, the seleno- and telluro-phosphorus ligands, is less well documented. This is despite the growing interest in using selenolates and tellurolates as precursors to semiconducting metal selenides and tellurides,[4] and also as new reagents for the synthesis of selenium- and tellurium-containing organics.[5] Furthermore, triorganophosphane tellurides have been employed as more reactive sources of tellurium than elemental tellurium metal itself in, for example, the low-temperature synthesis of transition metal tellurium clusters and nanoclusters.[6] We have been interested in the synthesis and characterisation of new selenolate and tellurolate complexes utilising the insertion reaction of elemental chalcogens into carbon−lithium[7] or heteroatom−lithium bonds[8] and have recently reported the synthesis and structural characterisation of a lithium selenophosphinite, $[Ph_2PSeLi\cdot TMEDA]_2$ **1** [TMEDA = $(Me_2NCH_2)_2$], a lithium diselenophosphinate, $[Ph_2PSe_2Li\cdot THF\cdot TMEDA]$ **2**, and a dilithium triselenophosphonate, $[(c\text{-}C_6H_{11})PSe_3Li_2\cdot 2TMEDA]$ **3** (Figure 1).[8] In these systems the ligands were shown to exhibit a variety of novel coordination modes to the lithium centres which differed from those exhibited by their thio-phosphorus counterparts. This observation has now led us to turn our attention to the corresponding tellurium and mixed selenium/tellurium analogues.

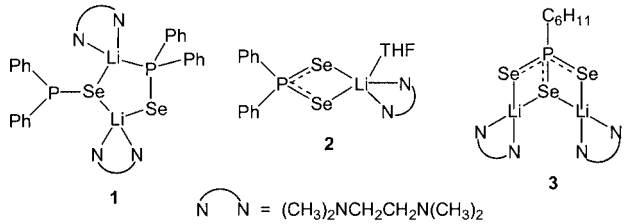

Figure 1. Lithium seleno-phosphorus complexes **1**, **2**, and **3**

Although the syntheses of ditellurophosphinates and selenotellurophosphinates have been reported previously by Sladky and Bildstein[9] there are to date no solid-state

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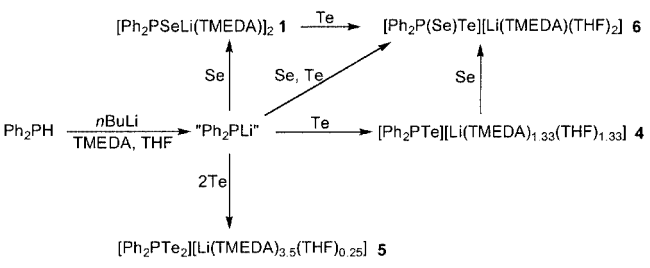
characterisations of these species. Indeed, a search of the Cambridge Structural Database[10] reveals fewer than twenty structures containing any form of phosphorus−tellurium bond, and of these the only metal-containing examples are the triorganophosphane telluride complexes $[(CO)_5WTeP{t}Bu_3]$[11] and $[(HgTeP{n}Bu_3)_3Br_5]_2$-$[Hg_2Br_6]$,[12] the tellurobisphosphane complex $[(CO)_4Cr(\mu$-$P{t}Bu_2)_2Te]$,[13] a 1,2,4-telluradiphosphole ring complex $[W(CO)_5(P_2TeC_2{t}Bu_2)]$,[14] a binuclear iron species $[Fe_2(CO)_6(\mu_2$-TeMes$)\{\mu_2$-P(iPr)TeMes$\}]$[15] and, most recently, a magnesium cyclodiphosphazane monotelluride $[{t}BuN(Te)P(\mu$-NtBu$)_2PN{t}Bu\cdot Mg(THF)_2]$.[16]

We present here the first solid-state characterisations of anionic telluro-phosphorus ligands, namely a tellurophosphinite $[Ph_2PTe][Li(TMEDA)_{1.33}(THF)_{1.33}]$ (**4**), a ditellurophosphinate $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (**5**), and a mixed chalcogen selenotellurophosphinate $[Ph_2P(Se)Te]$-$[Li(THF)_2(TMEDA)]$ (**6**). In addition we report on the reactions of dilithiated primary phosphanes with an excess of selenium. It has been shown previously that reaction of dilithio organylphosphides, $RPLi_2$, with elemental tellurium leads, via a series of phosphorus-phosphorus coupling reactions, to the formation of cyclic organylpolyphosphanes $(RP)_n$.[9] In contrast, reaction of $RPLi_2$ with three equivalents of selenium leads to formation of the dilithio triselenophosphonate **3**.[8] We now report how reaction of (c-C_6H_{11})PLi_2 with an excess (>3.2 equivalents) of selenium results in a single phosphorus-phosphorus coupling reaction to yield the novel tetraselenohypodiphosphonate complex $[\{(c$-$C_6H_{11})P(Se)(SeLi)\}_2\cdot 2TMEDA]$ (**7**).

Results and Discussion

Using a synthetic route analogous to that employed to prepare the seleno-phosphorus compounds **1** and **2**,[8] and also in accordance with literature procedures,[9] reaction of one equivalent of elemental tellurium with lithium diphenylphosphide in THF gave insertion of the tellurium into the phosphorus-lithium bond to yield the tellurophosphinite, $[Ph_2PTe][Li(TMEDA)_{1.33}(THF)_{1.33}]$ (**4**). Reaction of $LiPPh_2$ with two equivalents of elemental tellurium gave insertion followed by oxidation to yield the ditellurophosphinate $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (**5**). A mixed selenotellurophosphinate $[Ph_2P(Se)Te][Li(THF)_2$-$(TMEDA)]$ (**6**) was prepared from reaction of lithium diphenylphosphide with elemental selenium and tellurium in a one-pot reaction, although we were also able to prepare **6** from reaction of **1** or **4** with one equivalent of tellurium or selenium respectively (Scheme 1). All of these tellurium-containing compounds (**4**−**6**) are much more reactive than their selenium analogues (**1**, **2**), being highly air, moisture, and light sensitive, and readily decompose to deposit amorphous tellurium.



Scheme 1

X-ray structural analysis of $[Ph_2PTe][Li(TMEDA)_{1.33}(THF)_{1.33}]$ (**4**) shows it to crystallise as an ion-separated species consisting of the tellurophosphinite anion $[Ph_2PTe]^-$ and a solvated lithium cation (Figure 2); two different lithium cations are present in the crystal lattice, $[(TMEDA)(THF)_2Li]^+$ (67% occupancy, depicted in Figure 2) and $[(TMEDA)_2Li]^+$ (33% occupancy). The tellurophosphinite anion contains a distorted pyramidal phosphorus atom with angles of 97.8(1), 105.8(1) and 107.6(1)° (Table 1), the most "acute" corresponding to the Ph−P−Ph angle (i.e. between the two least sterically demanding substituents). The P−Te bond length of 2.447(1) Å is slightly shorter than previously reported P−Te single bonds: 2.565 Å (av.) in $[(i$Pr$)_2P]_2Te$;[17] 2.481(1) and 2.491(1) Å in $[(CO)_4Cr(\mu$-PtBu$_2)_2Te]$;[13] 2.4728(9) and 2.4790(5) Å in the phosphorus-tellurium cage $P_6C_4{t}Bu_4Te$.[18] This shortening suggests that the species exists predominately as its Ph_2P-Te^- tautomer with a P−Te single bond and the negative charge localised on the tellurium centre, with possibly some minor contribution from the $Ph_2P(=Te)^-$ tautomer resulting in a slight shortening of the P−Te bond. Given the weakness of phosphorus−tellurium double bonds[1c] it is perhaps not unexpected that the equilibrium lies well on the side of the Ph_2P-Te^- tautomer and this is also in agreement with our observations with the selenium analogue **1**, which also exists in a similar tautomeric form.[8] The ^{31}P NMR spectrum of **4** consists of a single peak with ^{125}Te satellites ($^1J_{P,Te}$ = 747 Hz). As expected the coupling constant is approximately two to three times larger than the corresponding P−Se coupling constants in **1**, and is also at the top end of the range of values expected for P−Te single bonds (reflecting the slightly shorter P−Te distance), for example 451 Hz in $({t}Bu_2P)_2Te$.[19] It is interesting to note the absence of any Te−Li or P−Li bonding interactions in the solid-state structure of **4**, especially when compared to the analogous Se complex **1** where two distinct coordination modes were observed: end-on bridging from Se to two Li and side-on bridging from Se to one Li and P to another Li.[8] Low-temperature ^{31}P NMR spectroscopic studies were carried out on **4**, but even at −70 °C we were unable to verify the existence of any metal−tellurophosphinite bonding, there being only one constant peak observed as the temperature was lowered (cf. **1**[8]). Although lithium−tellurium bonds are expected to be weak due to the size mismatch of the atoms, Li−Te bonds have previously been reported in both Si−Te−Li[20] and C−Te−Li systems[7,20d,21] and, to the best of our knowledge, the only example of an ion-separated lithium tellurolate is $[(Me_3Si)_3$-$SiTe][Li(12\text{-crown-}4)_2]$ where the lithium cation is stabilised by crown ether ligands. It therefore seems likely that stabil-

isation of the negative charge on the tellurium by the phosphorus in **4** is responsible for the lack of Te−Li bonding, presumably due to the $Ph_2P(=Te)^-$ tautomer formed from donation of a lone pair in a p orbital on the tellurium into an empty d orbital on the phosphorus. However, it is also possible that overlap of the p orbitals on tellurium with σ* orbitals on the Ph_2P moiety is occurring, similar to that previously reported for triorganophosphane tellurides.[6,22] Both of these interactions would result in a shortening of the P−Te bond as observed in the solid state and in solution.

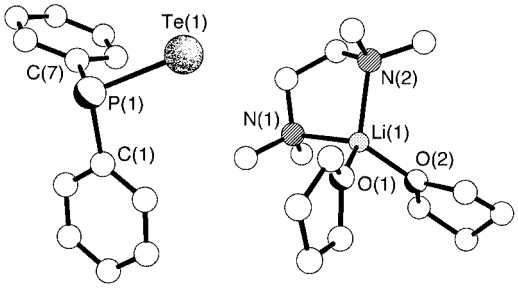


Figure 2. The molecular structure of $[Ph_2PTe][Li(TMEDA)_{1.33}(THF)_{1.33}]$ (**4**) showing the major occupancy $[(TMEDA)(THF)_2Li]^+$ cation

The solid-state characterisation of dark red crystals of $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (**5**) reveals an ion-separated species comprising a $[Ph_2PTe_2]^-$ anion and a combination of $[(THF)_4Li]^+$ (75%) and $[(TMEDA)(THF)_2Li]^+$ (25%) solvated lithium cations. The crystals contain two crystallographically independent cation-anion pairs in the asymmetric unit (see Figure 3 and Figure S1 (Supporting Information, see footnote on page 1 of this article); selected bond lengths and angles for the major component are given in Table 1). The phosphorus atoms in both of the independent anions in **5** are distorted tetrahedral with Te−P−Te angles of 118.6(2) and 117.3(2)°, and Ph−P−Ph angles of 100.6(5) and 101.8(6)°; the Ph−P−Te angles range between 107.9(4) and 110.3(5)°. The four P−Te bond lengths (av. 2.391 Å) do not differ significantly, ranging between 2.380(4) and 2.399(3) Å. These values are concordant with delocalisation of the negative charge throughout the ditellurophosphinate group and would suggest a formal bond order of 1.5 for each of the P−Te bonds, analogous to the bonding observed in lithium diselenophosphinates and di-

Table 1. Selected bond lengths [Å] and angles [°] for **4**−**7**

4	P(1)−Te(1)	2.4471(9)	P(1)−C(1)	1.857(8)
	P(1)−C(7)	1.851(3)		
	Te(1)−P(1)−C(1)	107.57(11)	Te(1)−P(1)−C(7)	105.78(10)
	C(1)−P(1)−C(7)	97.82(14)		
5	P(1)−Te(1)	2.399(3)	P(1)−Te(2)	2.380(4)
	P(1)−C(1)	1.843(8)	P(1)−C(7)	1.851(12)
	Te(1)−P(1)−Te(2)	118.56(15)	Te(1)−P(1)−C(1)	107.9(3)
	Te(1)−P(1)−C(7)	110.0(4)	Te(2)−P(1)−C(1)	110.1(3)
	Te(2)−P(1)−C(7)	108.2(4)	C(1)−P(1)−C(7)	100.6(5)
6	P(1)−Te(1)	2.379(3)	P(1)−Se(1)	2.137(6)
	P(1)−C(1)	1.847(5)	P(1)−C(7)	1.848(5)
	Te(1)−P(1)−Se(1)	116.8(2)	Te(1)−P(1)−C(1)	110.7(2)
	Te(1)−P(1)−C(7)	111.0(2)	Se(1)−P(1)−C(1)	110.5(3)
	Se(1)−P(1)−C(7)	106.7(3)	C(1)−P(1)−C(7)	99.8(2)
7	Se(1)−P(1)	2.0719(16)	Se(1)−Li(1)	2.561(4)
	Se(1′)−P(1)	2.2290(16)	Se(1′)−Li(1)	2.561(4)
	P(1)−C(1)	1.858(5)	P(1)−Se(1A)	2.0719(16)
	P(1)−Se(1D)	2.2290(16)	P(1)−P(1A)	2.2516(18)
	Li(1)−N(1)	2.084(6)	Li(1)−N(1B)	2.084(6)
	Li(1)−Se(1B)	2.561(4)	Li(1)−Se(1F)	2.561(4)
	P(1)−Se(1)−Li(1)	99.33(14)	P(1)−Se(1′)−Li(1)	95.24(13)
	C(1)−P(1)−Se(1A)	113.30(16)	C(1)−P(1)−Se(1)	91.16(15)
	Se(1)−P(1)−Se(1A)	120.10(9)	C(1)−P(1)−Se(1D)	126.81(16)
	Se(1)−P(1)−Se(1D)	116.33(5)	C(1)−P(1)−Se(1′)	104.20(15)
	Se(1A)−P(1)−Se(1′)	116.33(5)	Se(1D)−P(1)−Se(1′)	109.58(8)
	C(1)−P(1)−P(1A)	105.09(16)	Se(1A)−P(1)−P(1A)	112.24(5)
	Se(1)−P(1)−P(1A)	112.24(5)	Se(1D)−P(1)−P(1A)	104.61(5)
	Se(1′)−P(1)−P(1A)	104.61(5)	Se(1B)−Li(1)−Se(1′)	104.0(2)
	Se(1)−Li(1)−Se(1B)	104.6(3)	Se(1′)−Li(1)−Se(1F)	106.0(3)
	Se(1)−Li(1)−Se(1F)	104.0(2)		

thiophosphinates.[1,8] However, although these phosphorus−tellurium bonds are shorter than, for example, the P−Te single bond observed in **4** [2.447(1) Å], they do not differ considerably in length from formal "double" bonds [such as those in triorganophosphane tellurides, $TePR_3$, i.e. 2.368 Å in $TeP{t}Bu_3$,[23] 2.365 Å in $TeP{i}Pr_3$,[24] and 2.371 Å in $t{Bu}_2P(Te)NH(C_6H_{11})$[25]]. There has been considerable debate in the literature concerning the nature of the multiple bonding in phosphorus-tellurium compounds,[6] particularly the triorganophosphane tellurides, with ^{125}Te NMR and Mössbauer spectroscopy being interpreted as showing no P−Te multiple bonding in these compounds,[26] whereas density functional theory calculations have shown contributions from resonance structures consistent with substantial multiple bonding.[22] The P−Te bonds in **5** are the first crystallographically characterised P−Te bonds with a "formal" bond order of 1.5 (assuming complete delocalisation of the negative charge throughout the ditellurophosphinate) and therefore allow us speculate that, due to the similarity in bond lengths, the correct bond order for triorganophosphane tellurides is also 1.5. This conclusion agrees with the calculations carried out by Sandblom, Ziegler and Chivers.[22] It is also worthwhile noting that the ^{31}P NMR spectrum of **5** has a $^1J_{P,Te}$ coupling constant of 1530 Hz which is close to the range observed elsewhere for triorganophosphane tellurides (1548−1743 Hz),[19] indicating that the P−Te bonds in these two species are of similar length both in solution and in the solid-state ($^1J_{P,Te}$ coupling constants are known to correlate very strongly with bond lengths[19]).

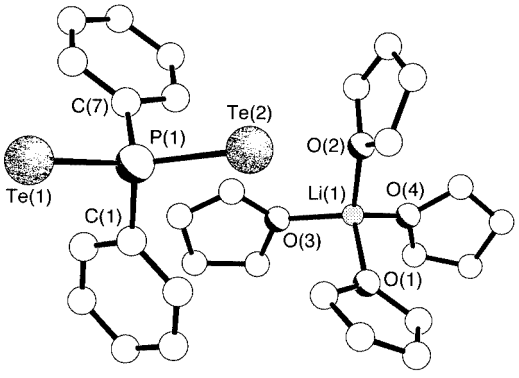


Figure 3. The molecular structure of one of the crystallographically independent cation:anion pairs present in the crystals of $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (**5**) showing the major occupancy $[(THF)_4Li]^+$ cation

Crystals of $[Ph_2P(Se)Te][Li(THF)_2(TMEDA)]$ (**6**) were shown by X-ray analysis to contain a mixed chalcogen selenotellurophosphinate anion (Figure 4). The positions of the Te(1) and Se(1) centres are sometimes reversed (ca. 63:37, see Figure S2), and this disorder means that the possibility of a certain amount of the diseleno and ditellurophosphinate species also being present in the crystal cannot be ruled out, though NMR spectroscopic data (see later) suggests that any contribution from these species is likely to be minor. Again the species is ion separated, this time containing a $[Li(THF)_2(TMEDA)]^+$ cation. The geometry at phosphorus is distorted tetrahedral with, for the major occupancy atoms, a Ph−P−Ph angle of 99.8(2)° and a Te−P−Se angle of 116.8(2)°; the other angles are in the range 106.7(3)−111.0(2)° (Table 1). The P−Se bond lengths of 2.137(6) to Se(1), and 2.136(8) Å to Se(1′), are similar in length to those observed in the diselenophosphinate **2** [2.141(1) and 2.147(1) Å][8] and the P−Te bonds of 2.379(3) to Te(1), and 2.378(6) Å to Te(1′), are similar to those observed in the ditellurophosphinate **4** (av. 2.391 Å). Together these bond lengths point to delocalisation of the negative charge over the selenotellurophosphinate group to give P−Se and P−Te bonds of order 1.5. This interpretation is further supported by ^{31}P NMR spectroscopy (Figure 5) which shows one main phosphorus peak ($\delta = -43.0$ ppm) with both ^{77}Se and ^{125}Te satellites and coupling constants similar to those observed in the dichalcogenophosphinates **2** and **5**; $^1J_{P,Se} = -635$ Hz and $^1J_{P,Te} = 1485$ Hz in **6** cf. $^1J_{P,Se} = -585$ Hz in **2** and $^1J_{P,Te} = 1585$ Hz in **5**. Small peaks (< 10%) can also be seen in the ^{31}P NMR spectra at $\delta = 24.0$ and -121.8 ppm due to the presence of the dichalcogenophosphinate species **2** and **5** respectively, which are present in equilibrium with the asymmetric species **6**.[9] Low temperature ^{31}P NMR spectroscopy of this mixture shows the signals at $\delta = 24$ and -122 ppm to increase in size (20% at −70 °C) due to the equilibrium being shifted more towards the symmetrical chalcogenophosphinates **2** and **5** at lower temperatures.

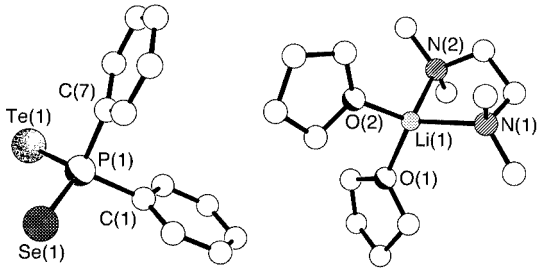


Figure 4. The molecular structure of $[Ph_2P(Se)Te][Li(THF)_2(TMEDA)]$ (**6**) showing the major occupancy orientation of the $[Ph_2PSeTe]^-$ anion

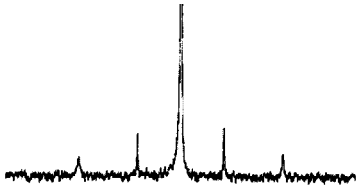
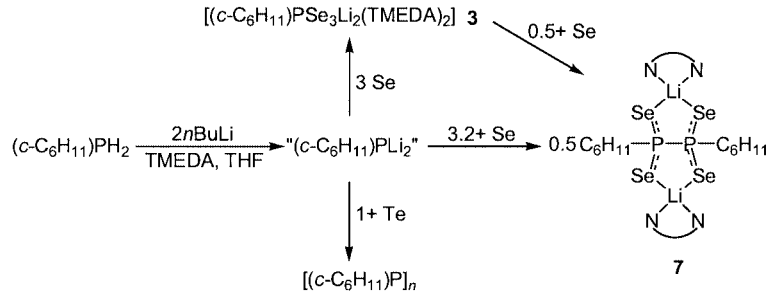


Figure 5. ^{31}P NMR spectrum of **6** showing the main truncated peak at $\delta = -43.0$ ppm with ^{77}Se and ^{125}Te satellites

Previously we have shown how reaction of dilithiated primary phosphanes, $RPLi_2$, with three equivalents of elemental selenium gives triselenophosphonates such as **3**. However, similar attempts to prepare tritellurophosphonates from reaction of $RPLi_2$ with elemental Te failed, instead forming cyclic poylphosphanes $(RP)_n$ and lithium telluride



Scheme 2

(Li_2Te_n) (Scheme 2). We therefore turned our attention to the reaction of $CyPLi_2$ and a greater than threefold excess of selenium powder to see if similar phosphorus-phosphorus coupling reactions[27] would occur. Indeed, reaction of $CyPLi_2$ with a greater than threefold excess of selenium was observed to give the dilithium tetraselenohypodiphosphonate complex [{(*c*-C_6H_{11})P(Se)(SeLi)}$_2$·2TMEDA] **7** via reduction of **3** with concomitant elimination of Li_2Se_n (Scheme 2), as well as some cyclic phosphane by-products. It also proved possible to prepare **7** by direct reaction of the triselenophosphonate **3** with 0.5 equivalents of selenium verifying that **3** is indeed an intermediate in this reaction. Further tests showed the reaction to proceed from (*c*-C_6H_{11})PLi_2 to **7** with between three (with reflux) and six equivalents of selenium, although the best yields with least contamination from cyclic polyphosphanes (<5% by ^{31}P NMR spectroscopy) were achieved with 3.2 equivalents of selenium at room temperature. There is only one other published example of a tetraselenohypodiphosphonate, that of the diphenyl analogue formed from the reaction of LiP(Ph)$SnPh_3$ (itself prepared from the reaction of PPh_5 with $LiSnPh_3$) with four equivalents of selenium, although no solid-state characterisation was reported and there was significant contamination with cyclic phosphanes (57%).[28]

X-ray structural characterisation of [{(*c*-C_6H_{11})P(Se)(SeLi)}$_2$·2TMEDA] (**7**, Figure 6) showed it to be disordered about a crystallographic C_{2h} position (with the twofold axis passing along the Li···LiA vector and the mirror pane bisecting the two Se−P−Se angles). As a consequence only the phosphorus, lithium, and nitrogen centres are ordered. In particular, each of the selenium centres is disordered over two 50% occupancy sites (shown in Figure S3, see Supporting Information) so that there are two distinctly different P−Se bond lengths [2.072(2) and 2.229(2) Å]; by contrast, all of the Li−Se distances are the same (Table 1). The 50:50 nature of this disorder means that for each of the two phosphorus centres it is crystallographically impossible to distinguish between i) the disorder of a single PSe_2 unit having one "short" and one "long" P−Se linkage, and ii) the superimposition of two different PSe_2 units, one that has two "short" P−Se linkages and one in which both bonds are "long". Although the presence of this disorder precludes an in-depth analysis of the bond lengths and angles, the structure clearly shows two lithium coordination sites on either side of the phosphorus-phosphorus backbone with each lithium bonding to two selenium atoms (one from each of the diselenophosphinate groups) and a TMEDA molecule, whilst the two cyclohexyl groups are in an *anti* conformation to one another. The two P−Se bond lengths are very disparate (differing by ca. 0.16 Å) with the longer bond [2.229(2) Å] being close to the length expected for a P−Se single bond [cf. P−Se bond lengths of 2.233(1) and 2.200(8) in **1**][8] and the shorter [2.072(16) Å] being within the range expected for a P−Se double bond.[29] This therefore suggests disorder of type i) with one selenium singly and one doubly bonded to each phosphorus atom and no, or very little, charge delocalisation occurring within the diselenophosphinate moieties. This behaviour therefore contrasts with that observed for the dichalcogenophosphinate groups in **2**, **5**, and **6** where complete charge delocalisation was present. The P−P bond, 2.252(2) Å, is in the range expected for a single bond (2.20 to 2.35 Å);[27] the Li−Se distances are all equal at 2.561(4) Å and are similar to previously reported Li−Se bond lengths in lithium seleno-phosphorus complexes.[8] Characterisation in solution by ^{31}P NMR spectroscopy showed just one predominate phosphorus signal (δ = 53.4 ppm) with satellites exhibiting AA′X splitting (where A is ^{31}P and X is ^{77}Se) due to the 23.9% abundant ^{77}Se isotopomer (Figure 7, a). ^{77}Se NMR spectroscopy also reveals an AA′X splitting pattern due to the same isotopomer (Figure 7, c). These ^{31}P and ^{77}Se NMR spectra correlate very accurately with compu-

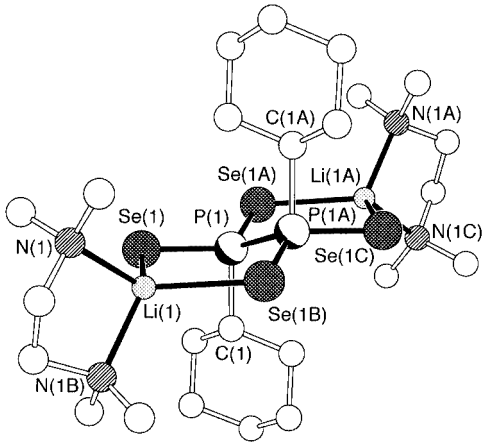


Figure 6. The molecular structure of [{(*c*-C_6H_{11})-P(Se)(SeLi)}$_2$·2TMEDA] (**7**)

tationally simulated spectra (Figure 7, b and d) with assignment iterated coupling constants of $^1J_{P,Se} = -623.2$, $^1J_{P,P} = -175.2$ and $^3J_{P,Se} = 2.0$ Hz (± 0.2 Hz).[30] The value of the $^1J_{P,Se}$ coupling constant is indicative of a phosphorus-selenium bond of order 1.5 and is similar to the $^1J_{P,Se}$ values observed for **2** (−585 Hz) and **6** (−635 Hz). Therefore, in contrast to the behaviour observed for **7** in the solid state, in solution all P−Se bonds are of equal length (on the NMR time scale), signifying that charge delocalisation within the diselenophosphinate groups is now taking place. The P-P NMR coupling constant is within the range expected for a single bond.[27]

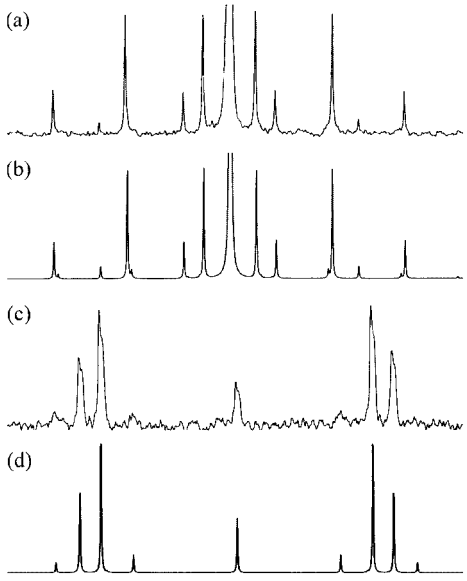


Figure 7. (a) ^{31}P NMR spectrum of **7** in C_6H_6; (b) Computationally simulated[30] ^{31}P NMR spectrum of **7**; (c) ^{77}Se NMR spectrum of **7** in C_6H_6; (d) Computationally simulated[30] ^{77}Se NMR spectrum of **7**

Conclusion

In summary, we have shown the first solid-state characterisations of a tellurophosphinite complex **4**, a ditellurophosphinate complex **5** and a mixed chalcogen selenotellurophosphinate complex **6**. Although these compounds are all ion-separated species with solvated lithium cations and therefore do not exhibit such a range of coordination modes with lithium as observed for their selenium or sulfur analogues, they do provide some valuable and rare structural insights into phosphorus tellurium multiple bonding. We are now investigating the coordination chemistry of these ligands with a range of transition metal centres as it is envisaged that stronger ligand-metal coordination will render these ligands more stable, and such complexes would be of potential use as chemical vapour deposition (CVD) precursors to metal chalcogenolides.[4] Related phosphinotellurgenoic amidato complexes [M{tBu$_2$P(Te)NR}$_2$] (M = Fe, Mn, and Co) have already shown promise is this area as suitable agents for the gas-phase deposition of metal chalcogenolide films.[31]

In addition we have demonstrated a new, clean synthetic route to a tetraselenohypodiphosphonate complex by reaction of dilithiated primary phosphanes with greater than three equivalents of elemental selenium, and have presented the first full characterisation of such a species. The tetradentate nature of these ligands should allow them to form wide range of coordination compounds and we are currently investigating their transmetallation reactions.

Experimental Section

General Procedures: All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen or argon using standard double manifold and glove-box techniques. Purification and drying of the solvents were done using standard methods.[32] Ph_2PH and $CyPH_2$ were purchased from Strem and all other chemicals from Lancaster.

NMR spectra were recorded on either a Bruker DPX400 (^{1}H and ^{31}P) or a Joel EX270 Delta Upgrade (^{77}Se and low temperature ^{31}P) spectrometer. External standards used were TMS (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) or Me_2Se (^{77}Se). Melting points were measured in sealed capillaries under argon.

Synthesis of [Ph$_2$PTe][Li(TMEDA)$_{1.33}$(THF)$_{1.33}$] (4): nBuLi (1.6 M in hexanes, 3.2 mL, 5 mmol) was added to Ph_2PH (0.86 mL, 5 mmol) and TMEDA (1.0 mL, 6.7 mmol) in 5 mL THF. The resulting solution was then transferred onto powdered Te (0.64 g, 5 mmol) in 3 mL of toluene at −78 °C and allowed to warm slowly to room temperature to give a dark red solution which was filtered through celite and left at −30 °C for 48 h to yield red crystals of **4** (1.52 g, 54%). M.p. 76−78 °C. Note that 0.66 THF was lost from **4** during the isolation procedure in the glove-box, so all spectroscopic characterisation is for [Ph$_2$PTe][Li(TMEDA)$_{1.33}$(THF)$_{0.67}$]. ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 1.74 (m, 2.7 H, THF), 2.09 (s, 16 H, TMEDA), 2.25 (s, 5.3 H, TMEDA), 3.59 (m, 2.7 H, THF), 6.97−7.63 (m, 10 H, Ph_2P-) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 25 °C): δ = 145.7, 134.0, 126.9, 125.7 (Ph_2P-), 67.1 (THF), 57.3, 45.6 (TMEDA), 25.2 (THF) ppm.^{31}P NMR (162 MHz, [D$_6$]DMSO, 25 °C): δ = −32.5 (s + d satellites, $^1J_{P,Te}$ = 747 Hz) ppm. $C_{22.66}H_{36.66}LiN_{2.66}O_{0.66}PTe$ (522.7): calcd. C 52.08, H 7.07, N 7.15; found C 51.99, H 6.98, N 7.18.

Synthesis of [Ph$_2$PTe$_2$][Li(THF)$_{3.5}$(TMEDA)$_{0.25}$] (5): nBuLi (1.6 M in hexanes, 1.6 mL, 2.5 mmol) was added to Ph_2PH (0.43 mL, 2.5 mmol) in 5 mL of THF. The resulting solution was then reacted with a suspension of powdered Te (0.64 g, 5 mmol) in 5 mL of THF at −78 °C followed by further stirring for 12 h at room temperature to give a dark red-brown solution. This solution was filtered through celite and reduced in volume to 5 mL in vacuo. Highly air- and moisture-sensitive dark-red crystals of **5** grew from this solution on storage at −30 °C over 72 h. Due to the extreme air, moisture and thermal instability of **5** we were unable to isolate it as a stable solid long enough to achieve full characterisation. Therefore ^{31}P NMR was carried out on a 1 mL aliquot of the reaction mixture to show qualitative production of **5**. ^{31}P NMR (162 MHz, THF, 25 °C): δ = −123.8 (s + d satellites, $^1J_{P,Te}$ = 1530 Hz) ppm.

Synthesis of [Ph$_2$P(Se)Te][Li(THF)$_2$(TMEDA)] (6): nBuLi (1.6 M in hexanes, 1.6 mL, 2.5 mmol) was added to Ph_2PH (0.43 mL, 2.5 mmol) and TMEDA (0.37 mL, 2.5 mmol) in 2 mL of toluene/2 mL of THF to give a clear yellow solution. This solution was then transferred onto a mixed suspension of Te powder (0.64 g,

Table 2. Crystal data, data collection and refinement parameters for compounds **4**−**7**

	4	**5**	**6**	**7**
Formula	$(C_{14}H_{32}LiN_2O_2)_{0.67}$-$(C_{12}H_{32}LiN_4)_{0.33}$-$(C_{12}H_{10}PTe)$	$(C_{16}H_{32}LiO_4)_{0.75}$-$(C_{14}H_{32}LiN_2O_2)_{0.25}$-$(C_{12}H_{10}PTe_2)$	$(C_{14}H_{32}LiN_2O_2)$-$(C_{12}H_{10}PSeTe)$	$C_{24}H_{54}Li_2N_4P_2Se_4$
Molecular mass	570.8	728.7	659.1	790.4
Crystal size [mm]	0.21 × 0.18 × 0.18	0.23 × 0.21 × 0.21	0.12 × 0.12 × 0.09	0.20 × 0.20 × 0.17
Temperature [K]	180	220	180	183
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	*Cmca* (no. 64)
a [Å]	15.7655(6)	15.974(3)	10.7603(10)	16.9716(8)
b [Å]	9.9042(3)	22.957(5)	12.0722(9)	12.4529(4)
c [Å]	18.6989(18)	17.372(4)	12.8144(12)	16.9878(10)
α [deg]	−	−	74.935(5)	−
β [deg]	91.150(2)	91.79(3)	76.817(4)	−
γ [deg]	−	−	73.593(4)	−
V [Å^3]	2919.15(18)	6367(2)	1520.3(2)	3590.3(3)
Z	4	8[a]	2	4[b]
D_c [g cm^{-3}]	1.299	1.520	1.440	1.462
Radiation used[c]	Mo-K_α	Mo-K_α	Mo-K_α	Cu-K_α[d]
μ [mm^{-1}]	1.09	1.91	2.25	5.87
2θ max [deg]	55.0	49.7	50.0	120.0
No. of unique reflns.				
Measured	6673	10763	5220	1367
Obsd., $\|F_o\| > 4\sigma(\|F_o\|)$	4381	6982	3458	1187
No. of variables	378	784	330	133
R_1, wR_2[d]	0.042, 0.105	0.097, 0.273	0.050, 0.098	0.029, 0.070

[a] There are two crystallographically independent cation:anion pairs in the asymmetric unit. [b] The molecule has crystallographic C_2h symmetry. [c] Details in common: graphite-monochromated radiation, refinement based on F^2. [d] Rotating anode source. [e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

5 mmol) and Se powder (0.40 g, 5 mmol) in 5 mL of THF at −78 °C, allowed to warm to room temperature slowly and stirred for a further 12 h. Orange crystals of **2** grew from this solution at room temperature over 72 h in 42% yield (1.39 g). M.p. 95−98 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 1.75 (m, 8 H, THF), 2.10 (s, 12 H, TMEDA), 2.27 (s, 4 H, TMEDA), 3.60 (m, 8 H, THF), 7.21−8.00 (m, 10 H, Ph$_2$P) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 25 °C): 142.0, 132.4, 128.5, 126.8 (Ph$_2$P-), 67.1 (THF), 57.3, 45.7 (TMEDA), 25.2 (THF) ppm. ^{31}P NMR (162 MHz, [D$_6$]DMSO, 25 °C): δ = 24.0 (5%, s + d satellites, $^1J_{P,Se}$ = −647; **2**), −43.0 (90%, s +2 × d satellites, $^1J_{P,Se}$ = −635, $^1J_{P,Te}$ = 1485 Hz; **6**), −121.8 (5%, s + d satellites, $^1J_{P,Te}$ = 1510; **5**) ppm. Due to contamination of **6** by small amounts of **2** and **5** we were unable to obtain satisfactory elemental analyses.

Synthesis of [{(*c*-C$_6$H$_{11}$)P(Se)(SeLi)}$_2$·2TMEDA] (7): *n*BuLi (1.6 M in hexanes, 3.2 mL, 5 mmol) was added to CyPH$_2$ (0.33 mL, 2.5 mmol) and TMEDA (0.75 mL, 5 mmol) in 4 mL of toluene/6 mL of THF at −78 °C. The resulting solution was then slowly warmed to room temperature and then transferred onto powdered grey Se (0.635 g, 8 mmol) and stirred for 15 min. Colourless crystals of **4** grew from the solution after 3 days at −27 °C 0.71 g, 72% yield). M.p. 166−168 °C. ^{1}H NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 0.82−2.10 (m, 11 H, C$_6$H$_{11}$), 2.12 (s, 4 H, TMEDA), 2.28 (s, 12 H, TMEDA) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 25 °C): δ = 57.3, 45.7 (TMEDA), 44.9, 27.3, 26.7, 26.5, 26.4, 26.3, 26.0 (*c*-C$_6$H$_{11}$) ppm. ^{31}P (109 MHz, [D$_6$]DMSO, 25 °C): δ = 53.4 (m) ppm. ^{77}Se (51.5 MHz, [D$_6$]DMSO, 25 °C): δ = −504 (m) ppm. $C_{24}H_{54}Li_2N_4P_2Se_4$ (790.4): calcd. C 36.47, H 6.89, N 7.09; found C 38.46, H 7.00, N 7.07.

X-ray Structure Determinations of 4−7: Table 2 provides a summary of the crystallographic data for compounds **4**−**7**. Data were collected on Nonius Kappa CCD (compounds **4**−**6**) and Siemens P4/RA (compound **7**) diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[33] The crystals of **4** contain two different cations, there being a ca. 67:33 mixture of [(TMEDA)(THF)$_2$Li]$^+$ and [(TMEDA)$_2$Li]$^+$. A similar situation is seen in the crystals of **5**, though here the two cations [(THF)$_4$Li]$^+$ and [(TMEDA)(THF)$_2$Li]$^+$ are present in a ca. 75:25 ratio. In the structure of **6** the positions of the Te(1) and Se(1) centres are occasionally reversed (ca. 63:37). The structure of **7** is substantially disordered about the crystallographic C_{2h} position (refinement in lower symmetry space groups does not remove the disorder) such that only the P(1), Li(1), and N(1) positions are ordered.

CCDC-208127−208130 (**4**−**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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