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Tuneable tetrel bonds between tin and heavy pnictogens†

Sachin Liyanage,[a] Jeffrey S. Ovens,[a] Steve Scheiner *[b] and David L. Bryce *[a]

The first example of a binary cocrystal, comprised of $SnPh_3Cl$ and PPh_3, whose components are organized *via* short and directional tetrel bonds (TtB) between tin and phosphorus, is described. DFT elucidates, for the first time, the factors influencing the strength of TtBs involving heavy pnictogens. A CSD survey reveals that such TtBs are also present and determinative in single component molecular systems, highlighting their significant potential as tuneable structure-directing elements.

The design and development of new materials, new catalytic processes, and the myriad of other chemical applications often relies on the control of structural and dynamic features *via* non-covalent interactions. The most well-known of these include, *e.g.*, hydrogen bonds, but in recent years the concept of so-called secondary bonding interactions,[1] also known as σ-hole-based interactions,[2] has gained popularity. The σ-hole is an area of depleted electron density and elevated electrostatic potential which can act as a Lewis acid and receive electrons from another, electron donating, Lewis base moiety. The halogen bond is the prototypical example of this class of interactions,[3,4] but many analogous element-based interactions have also been identified, the most studied of which include chalcogen bonds,[5] pnictogen bonds,[6] and tetrel bonds.[7] These interactions are appealing for a variety of chemical applications owing to their tuneability (*e.g.*, substituents can act as electron-donating or withdrawing groups) and directionality (*i.e.*, the non-covalent bond tends to align predictably opposite the covalent bonds of the bond donating moiety).

The tetrel bond is one wherein a group 14 (tetrel, T = C, Si, Ge, Sn, Pb, Fl) element acts as an electron acceptor (Fig. 1(a)). Recent crystallographic surveys have highlighted the important role of tin tetrel bonds in controlling crystal packing arrangements.[8,9] For example, recent cocrystal engineering studies with triphenyltin chloride as a prototypical tin tetrel bond (TtB) donor have established its utility as a structure-directing element in cases where relatively light first-row atoms are used as the electron donors (*e.g.*, N, O).[10] Tetrel bonds have also been demonstrated as important in solution, for example in anion binding applications[11] and as model systems for understanding the S_N2 reaction.[12] Tetrel bonds are also established entities in the gas phase.[13] Extensive computational work with a focus on nitrogen-based electron donors has established the strength of such interactions *in vacuo*, as well as the role of steric crowding and structural deformations.[14–17]

The strength and utility of tetrel bonds involving a heavier pnictogen as the electron donor is an open question. In the case of halogen bonds, the use of heavier pnictogens such as P, As, and Sb as electron donors remains uncommon and has only recently been explored in a deliberate manner.[18–21] Their rarity may stem from the greater reactivity of compounds containing

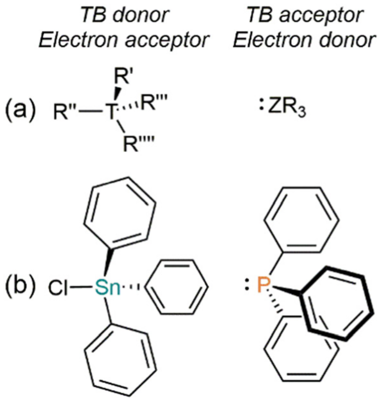

Fig. 1 Tetrel bond donors (left) and acceptors (right) considered in this work. (a): general formulae of donors and acceptors considered (T = tetrel element; Z = pnictogen element). (b) Molecular structures of compounds used to generate cocrystal **1**.

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[a] *Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, K1N6N5, Canada. E-mail: dbryce@uottawa.ca*

[b] *Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA. E-mail: steve.scheiner@usu.edu*

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these heavier pnictogens, relative to lighter amine electron donors. In this context, we sought to establish the viability of the tin-heavy pnictogen tetrel bond as a novel cocrystal engineering tool and structure-directing element in chemistry. Motivated by (i) the established applicability of $SnPh_3Cl$ as a robust TtB donor[10] and (ii) the viability of simple phosphines as 'heavy pnictogen' electron donors in halogen-bonded systems,[18,19] tetrel-bond directed cocrystallization of $SnPh_3Cl$ and PPh_3 was pursued as a first step (Fig. 1(b)).

Triphenyltin chloride (95%) and triphenylphosphine (99%) were obtained from ThermoFisher Scientific and Sigma Aldrich, respectively. In a typical procedure, 0.0140 g PPh_3 and 0.0202 g $SnPh_3Cl$ were dissolved in 6 mL chloroform and the solvent was subsequently allowed to slowly evaporate over a period of a few days. Colourless block shaped single cocrystals were collected and analyzed at 200 K *via* single-crystal X-ray diffraction using a Bruker APEX-II CCD instrument and MoKα radiation. The structure was solved using direct methods, and refined with full-matrix least-squares procedures based on $\boldsymbol{F}^2$ (see ESI†). The triphenyltin chloride triphenylphosphine cocrystal (**1**) features the two components in a 1 : 1 ratio.

As presented in Table 1, the structure packs in the $P\bar{1}$ space group and features a strong and directional tetrel bond between tin and phosphorus. This TtB is characterized by a distance of 3.541 Å and a nearly linear Cl–Sn···P angle of 171.4° (Fig. 2(a)). An end-on view of the TtB cocrystal, shown in Fig. 2(b), reveals a staggered conformation among the six phenyl groups, possibly to minimize steric contact upon TtB formation. The Sn···P distance is approximately 10% less than what is expected based on non-directional van der Waals (vdW) contact. The normalized distance parameter,[22] N_C, is calculated to be 0.89, where $N_C = d_{Sn\cdots P}/\Sigma r_{vdW}$; $d_{Sn\cdots P}$ is the experimental distance, and the denominator is the sum of the vdW radii of Sn and P. The value of this parameter, coupled with the highly directional nature of the contact, are consistent with the formation of a tetrel bond *via* donation of electron density from the phosphorus lone pair into the σ-hole opposite the Cl–Sn covalent bond on the tin atom. The metrics for **1** may be compared to those for analogous cocrystals of $SnPh_3Cl$ featuring lighter oxygen and nitrogen-based electron donors.[10] In those systems, N_C is closer to 0.60, signifying a shorter stronger contact, and the Cl–Sn···P angles range from approximately 170 to 180°, consistent with the geometry seen in **1**.

Density functional theory computations using the M06-2X functional[23] and the polarized triple-ζ def2-TZVP basis set were carried out using Gaussian 16[24] to assess TtB strength and geometry in a series of tin tetrel bonded systems involving heavier pnictogens as electron donors (see ESI†). The simple SnH_4 molecule was taken as a prototype Lewis acid with no substituents on the tetravalent Sn. As a first modification, its σ-hole was amplified by replacing one H atom by F. In another variation that makes this model more closely resemble the acid within cocrystal **1**, the Sn was surrounded by three methyl groups and a single Cl atom. Three pnictogen Z atoms (N, P, and As) were considered as electron donor atoms in their trivalent configurations. The three R substituents considered on these ZR_3 bases were H, F, and Me. Altogether, there were 24 different acid-base combinations considered here designed to cover a wide range of TtB strength.

Table 1 Crystallographic and structural details for **1** (*T* = 200 K)

Space group	$P\bar{1}$
Cell parameters	a = 10.949(3); b = 11.464(3); c = 12.442(3) Å
Cell angles	α = 90.554(7)°; β = 99.184(6)°; γ = 97.708(7)°
Sn···P distance	3.541 Å
Normalized contact, N_C	0.89
$\theta_{Cl\text{–}Sn\cdots P}$	171.4°

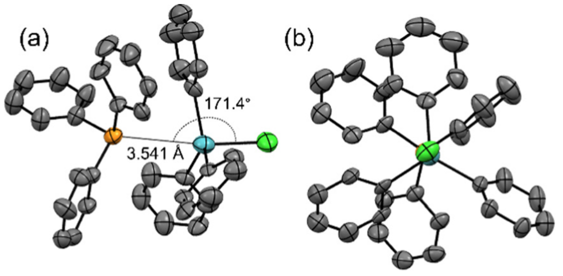

Fig. 2 ORTEP representations of the triphenyltin chloride–triphenylphosphine cocrystal (**1**). (a) Side view with TtB metrics; (b) view along the TtB axis. Sn: teal; P: orange; Cl: bright green; C: grey; hydrogen: not shown. CCDC 2266467.

The pairing of each Sn-containing Lewis acid with a ZR_3 base resulted in most cases in a clear TtB. The Z lone pair, as defined by the C_3 axis of the base, aligned closely with the extension of the R–Sn covalent bond, which in turn passes through the Sn σ-hole; the Sn···Z distance was shorter than the sum of the individual atomic vdW radii. AIM analysis of each of these complexes confirmed the presence of a Sn···Z bond path as the single path connecting the two units, and NBO analysis revealed the expected charge transfer from the Z lone pair to a σ*(SnR) antibonding orbital. In several of the more weakly bound complexes, however, this alignment was a poor one, and any Sn···Z bond path, if one existed at all, was augmented by weak secondary intermolecular paths, casting doubt on whether such a complex could legitimately be characterized as tetrel bonded. These questionable TtBs were those whose interaction energies were less than 2 kcal mol^{-1}, as described in more detail below.

The values of these interaction energies for various of these pairs are listed in Table 2, and display certain clear trends. The upper three rows of the table refer to SnH_4 as Lewis acid.

Table 2 Interaction energies ($-E_{int}$, kcal mol^{-1}) of tetrel-bonded complexes

TtB donor	TtB acceptor	Z = N	Z = P	Z = As
SnH_4	ZF_3	1.13	1.31	—
SnH_4	ZH_3	4.76	1.80	1.63
SnH_4	ZMe_3	8.51	3.67	3.17
$SnFH_3$	ZF_3	2.08	1.85	0.0
$SnFH_3$	ZF_2H	4.96	3.31	1.65
$SnFH_3$	ZFH_2	8.38	4.18	2.94
$SnFH_3$	ZH_3	12.27	4.77	4.12
$SnClMe_3$	ZMe_3	14.98	9.34	7.37

Without the benefit of an electron-withdrawing substituent, this acid has only a moderate σ-hole, with $V_{\max}$ = 23.5 kcal mol^{-1}, defined as the value of the electrostatic potential on a ρ = 0.001 au isodensity surface. It can form a clear TtB with NH_3, but such a bond is questionable for the heavier PH_3 and AsH_3, as these two base molecules rotate their lone pair away from the Sn···Z axis by more than 30°. Nonetheless, this TtB is affirmed by a Sb···Z AIM bond path and by NBO Z lone pair to σ*(SnH) charge transfer. In any case, whether true TtB or not, this interaction is quite weak.

Replacing the three H atoms on the base by electron-withdrawing F reduces the Z lone pair availability and essentially precludes a TtB of any magnitude with SnH_4, and even the presence of a TtB is itself questionable. For example, the AIM bond path connects the P/As with a H atom of SnH_4, rather than with Sn itself. On the other hand, SnH_4 engages in a robust TtB with all three trimethylated bases. Replacing one of the H atoms of SnH_4 by F doubles its σ-hole depth to 48.8 kcal mol^{-1}. This substituted acid is thus a much more effective electron acceptor, able to form a viable TtB with all bases, save the ZF_3 units. With each successive replacement of an F atom of ZF_3 by a H, this TtB grows progressively stronger, culminating in an interaction energy of 12.3 kcal mol^{-1} for $FH_3Sn\cdots NH_3$. Another clear trend apparent in the data is the weakening of the TtB as the Z atom grows larger: N > P > As. These patterns can be visualized more easily in Fig. 3 which displays the behaviour of the interaction energy for each Z atom as separate curves, where the clear superiority of N as base is readily apparent, as is the smaller decrement on going from P to As.

The last point on the far right of Fig. 3, and the last row of Table 2, refers to fully methylated acid and base, and with a Cl atom serving to amplify the σ-hole on the $ClSnMe_3$ unit. Together, these substitutions lead to a $V_{\max}$ of 46.1 kcal mol^{-1} for $SnClMe_3$, and to a quite strong TtB, even for Z = As. This system is a particularly faithful model of the novel cocrystal **1** that has been discussed above. For both the acid Sn and base P atoms, the phenyl groups to which they are attached have been simplified to methyl groups. As seen by the bottom entry of Table 2, the TtB in this system can be as strong as 9.3 kcal mol^{-1} if the entire complex is fully optimized. In order to more closely simulate the actual crystal of **1**, all of the non-H atoms in this complex were frozen in their X-ray coordinates, optimizing only the H atom positions. The main perturbation of this atom freezing is to elongate the optimized Sn···P distance from 3.290 to 3.541 Å. But even with this stretch, the TtB remains strong, decreasing by only 0.5 kcal mol^{-1} to 8.78 kcal mol^{-1}. π···π interactions between phenyl rings in **1** make only a minor contribution to the total binding between PPh_3 and $SnPh_3Cl$ (ESI†).

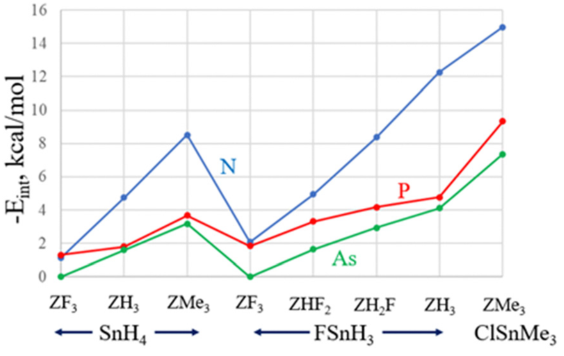

Fig. 3 Interaction energies of complexes pairing Sn Lewis acid with pnictogen (Z) base.

Table 3 Normalized Sn···Z distances (N_C)

TtB donor	TtB acceptor	Z = N	Z = P	Z = As
SnH_4	ZF_3	0.832	0.876	0.920
SnH_4	ZH_3	0.754	0.875	0.903
SnH_4	ZMe_3	0.696	0.843	0.872
$SnFH_3$	ZF_3	0.760	0.825	0.875
$SnFH_3$	ZF_2H	0.719	0.804	0.855
$SnFH_3$	ZFH_2	0.685	0.798	0.841
$SnFH_3$	ZH_3	0.661	0.800	0.833
$SnClMe_3$	ZMe_3	0.680	0.762	0.816

From a crystallographic perspective, a prime factor in distinguishing a noncovalent bonding attraction is the normalized contact distance N_C. These normalized distances are reported in Table 3 where they are all comfortably less than unity, buttressing the claim of a stabilizing TtB. In some of the stronger bonds, N_C drops below 0.7. These quantities are quite consistent with the interaction energies in Table 2, displaying very similar trends. The distances increase in the N < P < As order, just as the energies diminish, contract as F atoms on the base are swapped out for hydrogens, and also shorten when a F atom is placed on the acid.

The leading crystallographic reviews of tetrel bonds in solids[8,9] both focus largely on N, O, and halide electron donors and only mention phosphorus in passing.[9] Although cocrystal **1**, reported above, appears to be the first cocrystal to be purposely engineered on the basis of a tin-phosphorus tetrel bond, the generality of this motif may be further assessed *via* a survey of the Cambridge Structural Database (CSD) (Fig. S4; ESI†). The database was searched *via* Conquest software for all structures featuring tin-phosphorus distances between 2.50 and 4.00 Å. Note that the sum of the covalent radii of Sn and P is 2.46 Å and the sum of their vdW radii is 3.97 Å. The survey revealed 46 hits, 15 of which do not show characteristics of TtBs (*e.g.*, distances close to the sum of the covalent radii; no directionality along the extension of the covalent bond opposite Sn). Of the remaining 31 hits, none are cocrystals wherein distinct chemical entities have been brought together in the crystallization process as a result of a TtB to form a novel product. Instead, these hits show pure one-component molecular systems with probable intramolecular Sn···P tetrel bonds, as assessed by TtB distance, angle, and directionality. Published examples tend to discuss 'intermolecular coordination' of Sn and P in general terms, not in terms of tetrel bonds, if these interactions are discussed at all. In these 31 systems, the Sn···P distances range from 2.988 Å (N_C = 0.75) in an organometallic sandwich complex (refcode USUFOG[25]) to 3.917 Å (N_C = 0.99) in diphenyl {2-[(triphenylstannyl)methyl]phenyl}phosphane (FOWCOM[26]). It

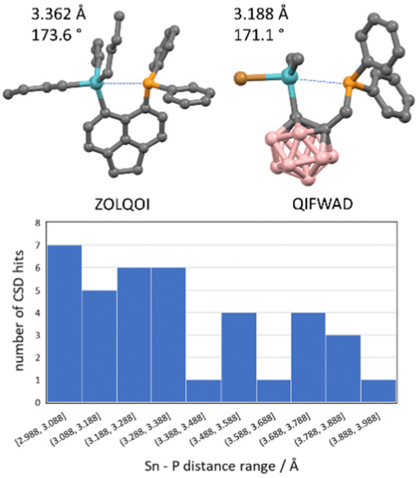

Fig. 4 Top: two examples of intramolecularly Sn···P tetrel bonded structures with distances and TtB angles shown. Colours as in Fig. 2; B: pink; Br: brown. Bottom: Histogram of Sn···P distances for likely TtBs (see text).

is instructive to highlight a few intramolecular examples which mirror the structural characteristics seen in **1**. For example, as shown in Fig. 4, entry ZOLQOI[27] contains a short intramolecular Sn···P tetrel bond with a distance of 3.362 Å and a nearly linear C–Sn···P angle of 173.6°. While the preorganization of the tin and phosphorus moieties arises from their proximate 1,3-substitution on the substituted naphthalene core, the highly directional nature of the Sn···P tetrel bond provides some indication that such interactions are present and determinative even in the absence of strong electron withdrawing groups. Entry QIFWAD[28] (Fig. 4) provides another interesting example of the ability of a Sn···P tetrel bond to organize and lock the conformation of substituents on a carborane core. Beyond molecular crystals, the role of Sn–P and Ge–P interactions in two-dimensional optoelectronic materials, SnP_3 and GeP_3, with possible photoconversion applications, has recently been demonstrated.[29]

In summary, we have described a first example of an expressly engineered cocrystal whose structure is governed by a strong and directional tin-phosphorus tetrel bond. DFT computations have established for the first time that while TtBs involving the heavier pnictogens (P, As) as electron donors tend to be weaker than those involving nitrogen atoms, a judicious tuning of electron-withdrawing substituents on the tetrel bond donor moiety can create the conditions for tin-heavy pnictogen tetrel bonds with interaction energies on the order of 10 kcal mol^{-1}. A survey of available X-ray diffraction structures has further confirmed for the first time the generality of the Sn···P tetrel bond and its determinative role in directing molecular conformation (thereby also indirectly affecting crystal packing) in the solid state. These conclusions suggest the applicability of tin-heavy pnictogen tetrel bonds as novel structure-directing elements in an array of areas in solid-state chemistry (*e.g.*, crystal engineering and materials design) and in solution (*e.g.*, homogeneous catalysis).

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Conflicts of interest

There are no conflicts to declare.

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