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Essay

The Inert Pair Effect: An Analysis Using the Chemdex Database

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Abstract

The presence of a so-called 'inert pair effect' in the chemistry of the 6p elements has been recognised for almost a century. Following a brief historical overview and a summary of the explanations that have been advanced to account for this effect, a more quantitative study of its prevalence and importance in the chemistry of these elements is presented based on an analysis of data in the recently published Chemdex database. These data clearly reveal a preponderance of lower valent compounds for the elements thallium, lead and bismuth and demonstrate that the various compound types exhibiting lower or higher valances are in accord with the published explanations.

Keywords: inorganic chemistry; p-block element chemistry; inert pair effect; Chemdex analysis

1. Introduction

What is nowadays referred to as the 'inert pair effect' in relation to the 6p elements of the periodic table was first discussed almost a century ago by Nevil Sidgwick in 1927 in his classic text, *The Electronic Theory of Valency* [1]. Thus, Sidgwick was aware that compounds of the elements thallium, lead and bismuth commonly exhibit valences of one, two and three that are, in each case, two less than the group maximum valence more often observed for the lighter members of the groups in which those elements reside (Groups 13–15). This observation (or effect) was attributed to an '*inert pair of electrons*' or '*. . .valency electrons*', specifically the 6s pair, although Sidgwick recognised that this attribution was no more than a description and was unable to offer an explanation for why this particular s pair should be more inert than other *n*s pairs in the p-block (Appendix A Note 1).

Perusal of a selection of current inorganic chemistry textbooks, some of which are referred to below, reveals that discussion of the inert pair effect generally features in descriptions of the chemistries of thallium and lead (and, to a lesser extent, bismuth). More particularly, comparisons are often made between the oxides and halides of these elements and those lighter members of their respective groups with lower atomic numbers. For example, with regard to the Group 14 elements, all of the divalent lead [or, in terms of oxidation states, Pb(II)] halides PbX_2 (X = F, Cl, Br, I) are known, whereas of the tetravalent [Pb(IV)] halides PbX_4, only the fluoride, PbF_4, is stable at room temperature [2] (Appendix A Note 2). The converse is true for the halides of carbon and silicon, where the tetrahalides are far more stable than the dihalides, whilst for germanium and tin, all of the dihalides and tetrahalides are isolable. It is interesting to note, however, that the situation concerning the lead halides is in contradistinction to the fact that tetravalent organo-lead compounds, PbR_4, are much more thermally stable than the corresponding divalent species, PbR_2, although such species can be isolated with R groups of sufficient steric bulk [2,3].

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The objective of this essay is to examine the general occurrence and importance of the inert pair effect in the chemistry of the 6p elements in relation to the chemistries of the 2p–5p elements through an interrogation of the recently published Chemdex database of compounds [4,5]. The results of this examination will be presented below, but first, it is instructive to briefly review some of the explanations that have been advanced to account for the existence of the inert pair effect.

The first attempt at a quantitative explanation of the inert pair effect was proposed by Drago in 1958 [6]. Drago understood that the 6s electron pairs of thallium and lead (the elements he considered in relation to their lighter congeners) are not inert in the sense that they are difficult to ionise since their ionisation energies are comparable to (indeed somewhat lower than) those of the *n*s electrons for some of the lighter members of their respective groups. The inert pair effect is therefore something of a misnomer in terms of the use of the word 'inert'. The explanation that Drago proposed, using available spectroscopic and thermodynamic data, was based on the relative magnitudes of electronic promotion energies and bond dissociation energies. Thus, if one considers the general reaction shown in Equation (1) (X = halide) for a Group 13 element M (where $n = 1$), the formation of the trivalent compound MX_3 requires that an electron in the 6s orbital be first promoted to a 6p orbital, i.e., $6s^2 6p^1$ to $6s^1 6p^2$. This process is the so-called promotion energy and is endothermic. For the lighter elements in the group, this promotion energy is more than recovered by the formation of the two extra M–X bonds. However, since covalent bond energies decrease (in the p-block) on descending a group, more so than the promotion energies vary, the situation for the 6p elements is that the formation of two much weaker M–X bonds is not sufficient to recover the necessary promotion energy. A similar argument was made for the Group 14 elements [Equation (1), $n = 2$], where the requisite promotion energy is associated with the electronic transition from $6s^2 6p^2$ to $6s^1 6p^3$ (Appendix A Note 3). Pertinent promotion energy and bond dissociation energy data for the Group 13 and 14 elements (excluding boron and carbon) are presented in Tables 1 and 2. Published values do vary according to the literature source (and no indication is given here of any experimental error in the values quoted), but the relative magnitudes of all the values are likely secure and sufficient to demonstrate the points that Drago made.

$$MX_n + X_2 \rightarrow MX_{n+2} \quad (1)$$

Table 1. Electronic promotion energies for the Group 13 elements ($6s^2 6p^1 \rightarrow 6s^1 6p^2$) and the Group 14 elements ($6s^2 6p^2 \rightarrow 6s^1 6p^3$) in kJ mol^{-1} [a].

Group 13	Promotion Energy kJ mol^{-1}	Group 14	Promotion Energy kJ mol^{-1}
Al	347	Si	399
Ga	454	Ge	502
In	418	Sn	474
Tl	541	Pb	607

[a] Values (quoted to 3 significant figures) are taken from ref. [7] and converted from original values in kcal mol^{-1}.

Table 2. Mean bond dissociation energies for bonds to chlorine for the elements Ga, In, Tl (monovalent and trivalent) and Ge, Sn, Pb (divalent and tetravalent) in kJ mol^{-1} [a].

M–Cl	Bond Dissociation Energy kJ mol^{-1}	M–Cl	Bond Dissociation Energy kJ mol^{-1}
Ga(I)–Cl	463	Ge(II)–Cl	385
Ga(III)–Cl	360	Ge(IV)–Cl	349
In(I)–Cl	435	Sn(II)–Cl	386
In(III)–Cl	328	Sn(IV)–Cl	323
Tl(I)–Cl	364	Pb(II)–Cl	304
Tl(III)–Cl	260	Pb(IV)–Cl	243

[a] Values are taken from ref. [8] with the exception of that for Ga(I)–Cl, which is taken from ref. [9].

A detailed computational study of the Group 13 hydrides and halides by Schwerdtfeger et al. in the early 1990s reached broadly similar conclusions to Drago, as is clear from their text reproduced below [10] (Appendix A Note 4) [11–14]. It is also worth noting that while Schwerdtfeger et al. considered the consequences of relativistic effects and spin–orbit coupling (both significant for thallium) together with the differences in bond energies between M(I)–X and M(III)–X for all the Group 13 elements (the former being stronger; see Table 2), none of these considerations were deemed to be dominant in accounting for the prevalence of lower valent (oxidation state) compounds in the chemistry of thallium and, by implication, other 6p elements [10].

> *We conclude that, at least for the compounds studied here, there is no special 6s inert pair effect. In short, the* ns^2 *pair is not especially inert for heavy element hydrides and fluorides. The low valency in the heavy element compounds arises naturally as a periodic trend towards weaker bonding, which cannot be explained either in terms of trends in atomic s ionization potentials or by s-p separations, but may be attributed to a decrease in metal–ligand covalent bond character, as suggested by Drago.*

In another similarly thorough computational study (also published in the early 1990s), Kaupp and Schleyer specifically compared and contrasted the inorganic and organometallic chemistry of lead [15]. Specifically, these authors reiterate that inorganic tetravalent lead [Pb(IV)] compounds are generally less stable and more reactive (often strongly oxidising) than corresponding divalent [Pb(II)] species, the converse being true for organometallic compounds. Furthermore, and as expected based on the statement in the preceding sentence, for the mixed species such as PbR_nX_{4-n} (R = organyl, X = halide), stability decreases as *n* decreases.

The calculations described by Kaupp and Schleyer confirm that tetravalent lead compounds are indeed destabilised by electronegative substituents (F and Cl in this study compared to H and Me) for reasons that they trace to the disparate radial extensions of the 6s and 6p orbitals. Thus, in an insightful 1984 review, Kutzelnigg drew attention to the fact that only for the 2s and 2p orbitals are the radial extensions similar [16]. For *n*s and *n*p orbitals where $n \geq 3$, the *n*p orbitals have a greater radial extension than the *n*s orbitals, the size discrepancy increasing with increasing *n*. The consequence of this size discrepancy is that s-p mixing (hybridisation) is increasingly disfavoured on descending a group (in the p-block) and that this process is accentuated as the degree of positive charge on the p-block element centre increases, attendant with an increasing electronegativity of the groups to which the element is attached. To quote specifically from ref. [15], (i) '*Consequently, the contribution of 6p-orbitals to covalent bonding in lead(IV) species becomes increasingly unfavorable when more electronegative substituents are present.*' and (ii), '*When these size differences increase,* sp^n *hybridization becomes increasingly unfavorable, and the covalent bonds will be weaker.*' (the difference between the dissociation energies of the Pb(II)–Cl and Pb(IV)–Cl bonds is evident from Table 2). The authors also state that the same explanation can be expected to apply

to Group 13, although in Group 15 it is noted that electronegative substituents are less destabilising for pentavalent bismuth. Whilst the thermal stability of PbF_4 would seem to be at odds with the explanation outlined above, the inherent strength of the Pb–F bonds is likely more than sufficient to offset the electronic promotion energy for lead deemed important in the explanations discussed by Drago and Schwerdtfeger et al. [6,10].

Of the many modern textbooks of inorganic chemistry that consider the inert pair effect, most reproduce the standard explanation based on the tension between electronic promotion energies and bond dissociation energies, albeit only in summary, but some offer rather more detailed analyses based on thermodynamic data including lattice energies, covalent bond energies and standard electrode potentials [8,17,18]. With regard to the last of these, selected standard electrode potential data for the Group 13 elements gallium, indium and thallium in acid solution are presented as Latimer diagrams in Figure 1a–c. In brief, the large positive values for the reduction of Tl^{3+} to either Tl^+ or Tl compared to the corresponding values for gallium and indium demonstrate that Tl^{3+} is much more easily reduced under these conditions than either Ga^{3+} or In^{3+}, a feature which is especially apparent when these data are displayed as the Frost diagram in Figure 1d.

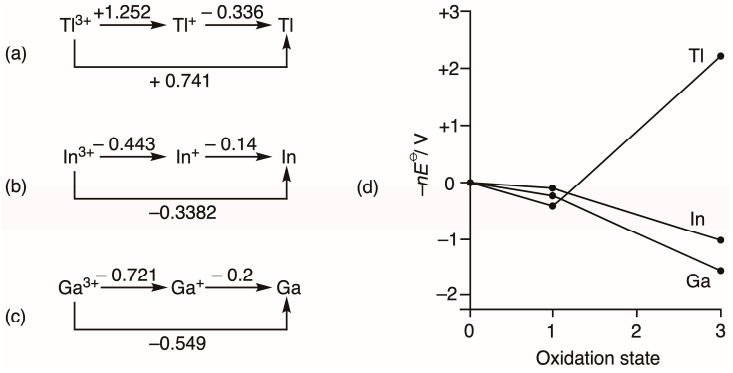

Figure 1. Latimer diagrams showing the standard reduction potentials (volts) in acid solution for the Group 13 elements, (**a**) thallium, (**b**) indium, (**c**) gallium; (**d**) a Frost diagram for all three elements displaying the same information. Data are taken from ref. [9].

With regard to the inert pair effect for Group 15, it is rather less marked for bismuth as noted by Kaupp and Schleyer [15]. Moreover, whilst several examples of penta-aryl bismuth compounds ($BiAr_5$) have been prepared, the corresponding triaryl species ($BiAr_3$) are thermally stable, unlike the lower valent aryls of lead and thallium. Of the pentavalent halides, however, only BiF_5 is thermally stable, and of the inorganic Bi(V) compounds that are known, many are strongly oxidising as expected [2].

As a consequence of their radioactivity and the short half-lives of their isotopes, the reported chemistry of the 6p elements polonium, astatine and radon is limited. In the case of polonium, examples of Po(II) and Po(IV) halides and oxides have been characterised, but the Po(VI) species PoO_3 and PoF_6 seem to have only a fugitive existence that is consistent with the presence of an inert pair effect for this element [2,19]. A recent computational study does consider the inert pair effect as part of the explanation for the reduced stability of RnO_4 compared with XeO_4 [20].

2. A Chemdex Database Analysis

Having briefly reviewed the history of the inert pair effect from its initial proposition to some of the explanations that have been offered, it is instructive to gain an appreciation of its generality in p-block element chemistry, especially in Groups 13–15, where its existence is most apparent. The recently published Chemdex database of compounds provides an opportunity for such a survey, the results of which are discussed below [4,5].

The data presented in Figure 2 reveal (in the form of a heat map), for each of the elements in Groups 13–15, the percentage of compounds in the database according to their valence number (VN) and their oxidation state (OS), and it is useful to consider each group in turn (Appendix A Note 5). For the elements of Group 13, the table that records the percentage of compounds according to the valence of the element [Figure 2a Valence numbers] clearly reveals a large preponderance of trivalent compounds for the elements boron, aluminium, gallium and indium but shows a marked increase in monovalent thallium compounds in accord with the expectation that the inert pair effect is an important feature in the chemistry of this element. Much the same picture is apparent when considering the OS values for the Group 13 elements such that for the vast majority of boron, aluminium, gallium and indium compounds, the OS is (III), whilst for thallium, a much higher proportion of compounds are Tl(I) [Figure 2a Oxidation numbers]. Those compounds for all the elements that are in oxidation states other than (I) and (III) reflect the difference between how valence and oxidation state are defined. Thus, taking Sidgwick's definition, the valence (or valence number, VN) assigned to an element is the number of electrons it uses in bonding [1]. In contrast, the oxidation state is defined according to the ionic approximation that therefore reflects the relative electronegativities of the elements concerned and whether or not a homonuclear element–element bond is present [21–25]. These issues are considered in more detail in refs. [23–25] and are specifically addressed below for carbon.

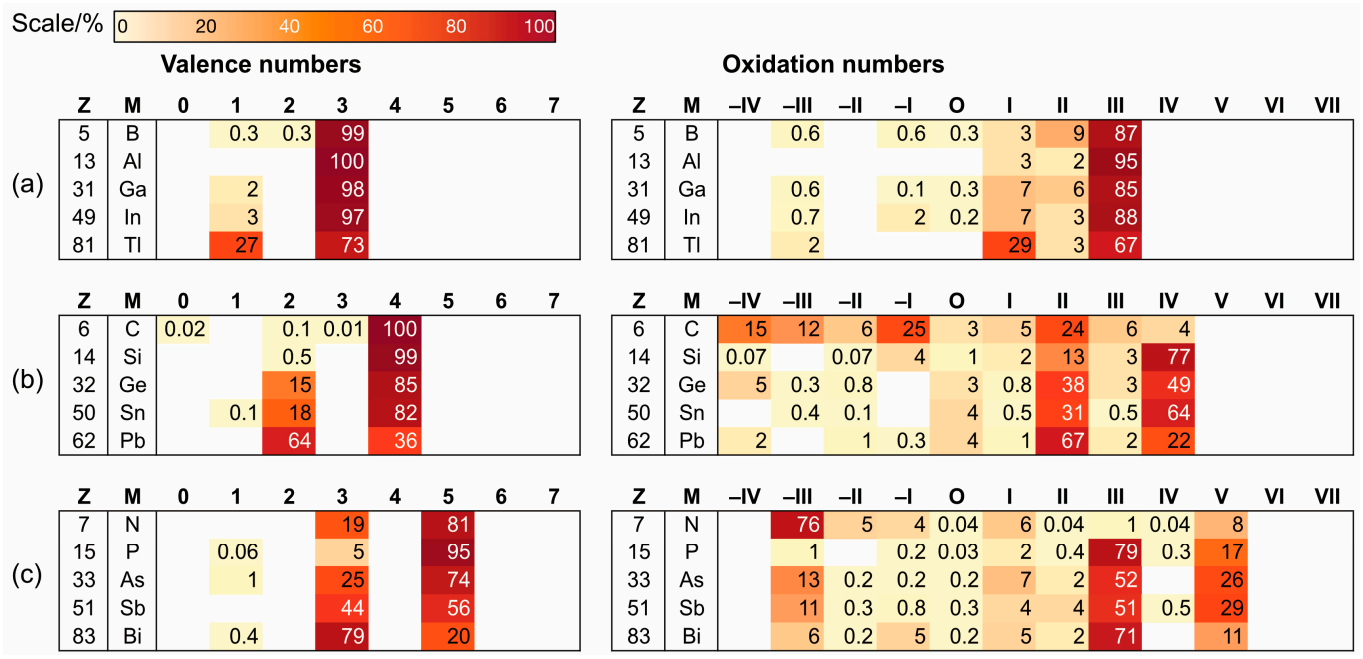

Figure 2. Data for the valence numbers and oxidation numbers (oxidation states in the text) of compounds of the elements of (**a**) Group 13, (**b**) Group 14 and (**c**) Group 15 presented as a heat map according to the percentage values (also shown) of entries in the Chemdex database [4,5] (Appendix A Note 5). Valence numbers are given in Arabic numerals and oxidation numbers/states in Roman numerals; Z is the atomic number of the element M.

The pros and cons of using VN or OS have been discussed previously and will not be reprised here, but the example of carbon in Group 14 shows that in terms of the discussion central to this topic, VN is rather more useful than OS [25–27]. Thus, Figure 2b reveals that essentially all carbon compounds are tetravalent [Figure 2b Valence numbers] (Appendix A Note 6), whereas the OS values for carbon span the range (–IV) to (IV) [Figure 2b Oxidation numbers]. This range of OS values reflects the fact that in its

chemistry, carbon is frequently present in molecules where it is bonded to elements that are less electronegative (usually hydrogen) or more electronegative (e.g., oxygen, nitrogen or halide) and often both. Moreover, in C–C-bonded species, the C–C bond is not considered when assigning the OS: for example, in C_2Cl_6, the carbon is formally in OS (III). For the heavier, more electropositive elements, the atoms to which the element is bonded are generally more electronegative, and M–M-bonded compounds are scarce, which is reflected in the fact that the two tables comprising Figure 2b increasingly resemble each other as the group is descended. Focussing, therefore, more on valence [Figure 2b Valence numbers], the importance of the inert pair effect in the chemistry of lead is immediately apparent compared even with tin and germanium and certainly in comparison with the chemistry of carbon and silicon.

Similarly, the data for Group 15 shown in Figure 2c reveal the importance of trivalence vs. pentavalence for bismuth in contrast to the lighter members of this group where the higher valent state is dominant [Figure 2c Valence numbers]. Oxidation states show a rather less obvious group trend, but this reflects how oxidation state is determined (see above) according to the atoms to which these elements are commonly bonded [Figure 2c Oxidation numbers].

Having looked at the general trends evident in the data presented in Figure 2, it is instructive to interrogate the data within the Chemdex database more closely in order to see which classes of compound comprise the individual categories for the elements thallium, lead and bismuth with, for the reasons given above, an emphasis on VN [4,5].

Monovalent thallium compounds typically comprise thallium bonded to a halide or pseudohalide or to a formally anionic ligand in which the donor atoms are oxygen or sulfur (sometimes nitrogen). Rather more ionic species include thallium(I) cations coordinated to ethers, including crown ethers and related *N*- and *S*-donor macrocycles. Notable by their absence, and in line with the discussion above, are any examples of σ-bonded alkyls or aryls, the only organometallic species being those in which a Tl(I) cation is coordinated to the π system of an arene or substituted cyclopentadienide ligand (Appendix A Note 7). Trivalent thallium compounds are also found in association with the same electronegative groups listed above for monovalent thallium, but a large proportion of compounds incorporate alkyl (usually methyl) and phenyl or other substituted aryl groups. This is again to be expected based on the discussion above, but an interesting category of compounds is those with the formula $[Tl(ML_n)_3]$, where ML_n is a formally anionic organotransition metal fragment. The low electronegativity of such groups is consistent with the arguments made by Kaupp and Schleyer that the higher valency compounds are more likely to be encountered with lower electronegativity groups.

The situation with lead chemistry is similar to that of thallium. Thus, in the majority of divalent lead compounds, the lead is bonded to a halide or pseudohalide or to a formally anionic ligand in which the donor atoms are oxygen or sulfur. There are several examples of compounds in which the atoms bonded to lead are nitrogen, silicon, germanium and selenium (usually with sterically bulky groups), but there is a dearth of examples featuring alkyls or aryls: two examples are the anion $[PbPh_3]^-$ and the compound $PbPh\{C_6H_3(C_6H_2Pr^i_3)_2\}$ with a sterically demanding aryl group. In contrast, the majority of tetravalent [Pb(IV)] compounds contain one or more alkyl or aryl groups, including several homoleptic species such as $PbPh_4$. Those species that do not contain an alkyl or aryl group are typically carboxylates, or compounds with related groups, and complexes with organotransition metal fragments such as $[Pb\{Co(CO)_4\}_4]$. The stability of the latter is consistent with the low electronegativity of the organotransition metal fragment as noted above for the thallium examples, and in this regard, it is interesting to highlight the species $[PbEt_{4-n}\{B(CN)_3\}_n]^{n-}$ (n = 1–4) that includes the stable tetra-anion $[Pb\{B(CN)_3\}_4]^{4-}$ in which

the lead is bound exclusively to electropositive boron centres. It is also interesting that whilst the tetravalent anion $[Pb\{B(CN)_3\}_4]^{4-}$ is stable, the corresponding divalent anion, $[Pb\{B(CN)_3\}_2]^{2-}$ is not, although the compound $Pb\{B(HCNDipp)_2\}_2$ (Dipp = 2,6-$Pr^iC_6H_3$) has been isolated and is an example of divalent lead bonded only to boron presumably as a result of steric stabilisation [28,29].

The chemistry of bismuth has much in common with that of thallium and lead, especially lead, but the most striking difference is that trivalent bismuth aryl compounds and their derivatives are much more thermally stable than the lower valent aryls of thallium and lead.

A final quantitative interrogation of the Chemdex database reveals the following for lead compounds. Thus, Chemdex contains a total of 185 entries for divalent lead and 104 entries for tetravalent lead, but what is interesting is that while only a little under 9% of divalent lead compounds have an attached carbon atom, the corresponding number is 42% for tetravalent lead. This is consistent with the discussion above that compounds of tetravalent lead show a preponderance of organometallic species in contrast to the chemistry of divalent lead. A similar result is apparent for bismuth, where 16% of trivalent bismuth compounds have attached carbon atoms (out of 423 entries) compared with 49% for pentavalent bismuth (out of 108 entries).

3. Conclusions

Following a brief historical overview of the inert pair effect and a summary of the explanations that have been offered to explain its origins, we have set out to provide, using the recently published Chemdex database, a more quantitative analysis according to the data presented in Figure 2 followed by a survey of the compound types for each of the salient elements in the valences/oxidation states they commonly adopt. The chemistry of the 6p elements thallium, lead and bismuth is relevant to many areas of current interest and application, and an understanding of characteristic features such as the inert pair effect is therefore important.

It is also instructive, however, to consider the inert pair effect from a pedagogical standpoint since it features in many teaching texts that cover the chemistry of the p-block elements. Thus, presenting the evidence for the inert pair effect and discussing its origins allow one not only to understand the effect itself but also to emphasise that some of the key features required to understand it have a much broader relevance. For example, the disparate radial extensions of the 6s and 6p orbitals are explained on the basis of Pauli repulsion, which is important in understanding many other aspects of p-block chemistry [30, 31]. Likewise with regard to the importance of relativistic effects in the chemistry of the heavier elements of the periodic table. Moreover, discussions concerning promotion energies can be seen in the wider context of electron reorganisation energies and their impact on the magnitude of bond dissociation energies as discussed by Schwerdtfeger, Frenking and co-workers [30].

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Appendix A. Notes

1. Sidgwick used the term 6_{11} rather than 6s. He also recognised the prior work of Grimm and Sommerfeld on the stability of s pairs of electrons, but the credit belongs to Sidgwick for bringing this matter to the attention of inorganic chemists.
2. $PbCl_4$ (a yellow oil) can be stored below 0 °C but decomposes to $PbCl_2$ and Cl_2 above 50 °C.
3. The electronic configurations $6s^16p^2$ for thallium and $6s^16p^3$ for lead following promotion of an electron from a ground state $6s^2$ configuration are sometimes referred to as the valence state.
4. For a subsequent study by Schwerdtfeger and co-workers that considered the thermodynamic and kinetic stability of the Group 13 trihydrides and covered a number of general points about the inert pair effect, see ref. [11], and for some early references (included in ref. [11]) to the importance of relativistic effects, see refs. [12] and [13]. Ref. [14] considers the electronegativity differences between Tl(I) and Tl(III) and between Pb(II) and Pb(IV), which are relevant to the values for the respective element–chlorine bond dissociation energies shown in Table 2.
5. Chemdex employs the term oxidation number (ON) rather than oxidation state (OS), although for the purposes of this paper, the two terms should be considered synonymous. Thus, while Figure 2 uses the term 'oxidation numbers' in the heading, the term oxidation state is employed in the text.
6. Examples of divalent carbon include *N*-heterocyclic carbenes (NHCs) and cyclic alkylamino carbenes (CAACs).
7. A survey of some other organothallium(I) species that have been reported is provided in ref. [11].

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