

Unusual geometries in main group chemistry

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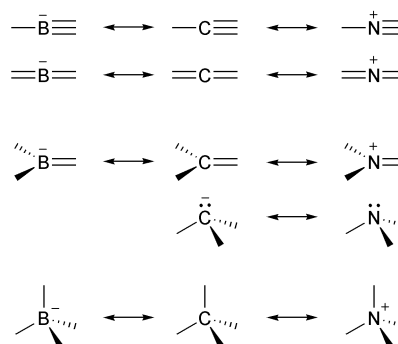
Over the past twenty five years, numerous heteroatom-containing analogues of classical organic moieties have been prepared and structurally characterized. The incorporation of group 13 to 15 heteroelements has often been reported to induce significant geometric distortions compared to the corresponding carbon compounds. These unusual geometries in main group derivatives are examined in this *tutorial review*, and the precise role of the heteroelements is discussed.

1 Introduction

Since the pioneering work of van't Hoff and Le Bel,¹ the understanding of the spatial arrangement of organic molecules has attracted considerable attention.² One of the most spectacular achievements is certainly the enforcement of inverted tetrahedral³ as well as planar⁴ geometries for tetracoordinate carbon compounds. Over the past twenty five years, heavier analogues of commonly found organic moieties have been the subject of numerous experimental and theoretical investigations. These studies have led to the discovery of a broad variety of new compounds featuring peculiar electronic structures and/or unusual geometries. This overview highlights the geometric distortions reported for derivatives featuring group 13 to 15 elements, compared to the related carbon species. Di-, tri- and tetra-coordinate compounds are successively considered, but hyper-valent compounds are not included.

The geometry of the molecules is intimately related to their electronic structure. This is clearly seen by considering the model of Gillespie, which is based on *valence-shell electron-pair repulsion* (VSEPR) and affords a qualitative estimation of the spatial arrangement of the atoms within molecules. This very simple model is applicable to a broad range of compounds (from carbon to main-group elements, and to some extent, even to transition metals). The geometry of molecules is also conveniently discussed by drawing comparisons between *isoelectronic systems*, *i.e.* between compounds with the same number of electrons. This is

illustrated in Scheme 1 for di-, tri- and tetra-coordinate compounds featuring second row elements. Moreover, this helpful principle can



Scheme 1

be extended to *valence isoelectronic systems*, *i.e.* to compounds with the same number of electrons in their valence shell. Accordingly, carbon moieties can be related not only to their boron and nitrogen analogues, but also to heavier group 13 to 15 derivatives.

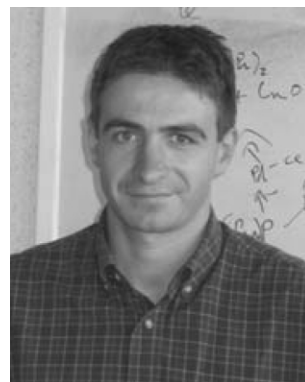
Among the specific properties⁵ of heavier main group elements, their size, their reluctance for s-p hybridization and for multiple bonding clearly play a central role in the reported unusual geometries, and are thus briefly discussed hereafter. Firstly, it is well known that 3rd to 6th row elements are significantly larger than

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their 2nd row analogues, as depicted schematically in Fig. 1. In fact, the covalent radii increase considerably from the 2nd to the 3rd row

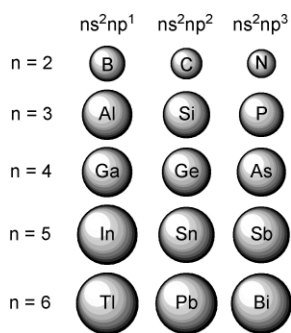


Fig. 1 Schematic representation of the size of 2nd to 6th row atoms.

(by *ca.* 50%), and to a lesser extent, from the 4th to the 5th row (by *ca.* 17%). The size of the atoms has of course considerable impact on their electronic properties, but may also have direct structural consequences, as described for cage compounds in section 4.1.

Secondly, heavier main group elements are reluctant to undergo hybridization. This electronic peculiarity can be schematically rationalised by considering the mixing of s and p atomic orbitals. The formation of hybrid orbitals mainly depends on two parameters (Fig. 2): the energy separation between the interacting orbitals,

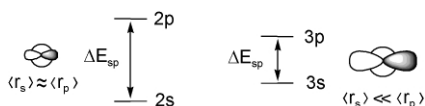


Fig. 2 Schematic representation of the s-p energy separation and orbital sizes for 2nd and 3rd row elements.

namely ΔE_{sp} , and their overlap. On the one hand, the promotion energy ΔE_{sp} decreases down a group, and the hybridization should thus be strengthened. On the other hand, 2s and 2p orbitals have similar sizes, whereas p orbitals are much more diffuse than s orbitals for heavier elements, and the s-p overlap thus decreases down a group. In fact, the overlap term appears to be prominent, meaning that s-p hybridization is less effective for heavier elements.

This phenomenon, usually referred to as *non-hybridization*, plays a central role in the chemistry of heavier main group elements. Indeed, lone pairs feature increased s-character, and are therefore relatively inert. This *inert pair* or *lone pair effect* is accompanied by the decreased availability of the valence electrons for bonding. As a result, heavier main group elements have a marked tendency for low valence states. The reluctance for hybridization also plays an important role in the inversion of pyramidal tricoordinate derivatives. Indeed, the activation barrier corresponds to the energy required to achieve the sp^2 -hybridized transition state, that is to say the energy required for the planarization of the central element (Fig. 3). Accordingly, phos-

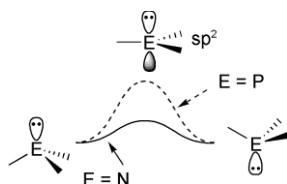


Fig. 3 Schematic representation for the inversion of pyramidal tricoordinate derivatives.

phines have significantly larger inversion barriers (30–35 kcal mol⁻¹), and therefore higher configurational stabilities, than amines (about 5 kcal mol⁻¹).

Thirdly, heavier main group elements are reluctant to form multiple bonds, as recognized early on by Pitzer and Mulliken,⁶ and

usually referred to as the *double-bond rule*. As expected, both σ - and π -bonds usually decrease in strength going down a group, as illustrated for carbon, silicon and germanium in Fig. 4. It is

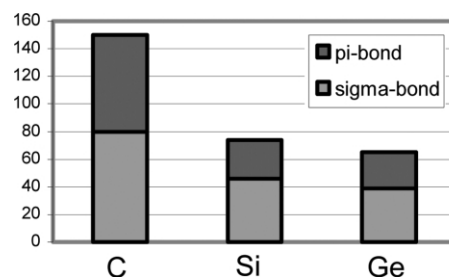


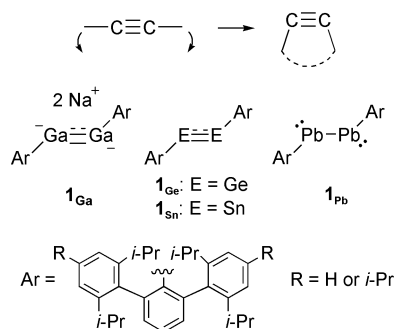
Fig. 4 Schematic representation of the homonuclear σ - and π -bond strengths (in kcal mol⁻¹) for carbon, silicon and germanium.

noteworthy that π -bonds are only slightly weaker than σ -bonds for carbon, whereas silicon and germanium form π -bonds of only half the strength of the corresponding σ -bonds. At a first glance, the weakness of π -bonds featuring heavier main group elements might be correlated to less efficient orbital overlap, but it has been more accurately attributed to enhanced inter- and intra-atomic Pauli repulsions.⁷ To circumvent this weak π -bonding, heavier elements may adopt unusual geometries, as in the case of heavier analogues of alkynes and alkenes discussed in sections 2.1 and 3.3, respectively.

2 Dicoordinate compounds: from linear to bent structures

2.1 Alkyne analogues

For alkynes, distortions from the linear geometry remain very rare and most often result from *syn*-bending due to ring strain.⁸ The weakness of multiple bonds between heavier main group elements has so far limited the number of stable triple-bonded compounds to just a few examples. All the reported alkyne analogues⁹ feature bulky aryl substituents and adopt a planar *trans*-bent geometry (Scheme 2). The bond order is of about 2.5 for the gallium,



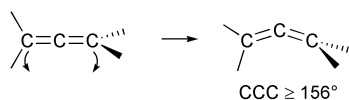
Scheme 2

germanium and tin derivatives **1_{Ga}**, **1_{Ge}** and **1_{Sn}**, which can be considered to some extent as gallyne, germyne and stannyne, but of only *ca.* 1 for the related lead compound **1_{Pb}**, which is best described as a diplumbylene. These unusual geometries have been demonstrated to result from a delicate interplay between π -bonds (in linear structures) and enhanced σ -bonds with localized lone pairs (in bent structures).

2.2 Allene analogues

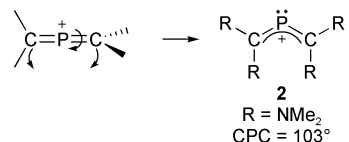
Several factors (ring strain, torsional strain, packing effect and orbital interaction) have been demonstrated to enforce distorted geometries for allenes, with bending at the central atom down to 156° (Scheme 3).¹⁰

Replacement of the central carbon by a phosphorus atom does not result in the hypothetical 2-phosphonio-allenic cation, but rather in the 2-phosphaallyl cation, as observed for compound **2**

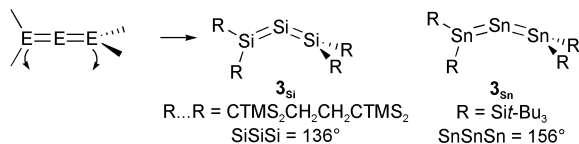


Scheme 3

(Scheme 4).¹¹ The strong bending (CPC = 103°) results from the reluctance of phosphorus to undergo s-p hybridization, while the coplanar arrangement of the two CR₂ fragments allows for allylic



Scheme 4



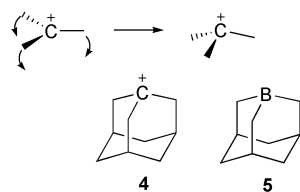
Scheme 4

π -delocalization. A similar, albeit less pronounced, bending has been reported for trisila- and tristanna-allenes **3_{Si}** and **3_{Sn}**.¹² The two ER₂ fragments do not deviate substantially from the usual perpendicular arrangement, but the terminal heavier elements are in slightly pyramidalized environments (as quantified by the sum of the three bond angles $\Sigma\alpha = 345\text{--}355^\circ$ compared to 360° for a planar geometry).

3 Tricoordinate compounds

3.1 Carbocation analogues: from trigonal planar to pyramidal environments

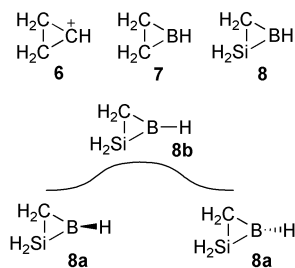
Preference for the trigonal planar arrangement in carbenium ions remains one of the tenets of organic chemistry, that has only been challenged in bridgehead positions of highly constrained systems such as the 1-adamantyl cation **4** (Scheme 5).¹³



Scheme 5

So far, the stabilization of tricoordinate pyramidal boron centres has only been investigated computationally. Not surprisingly, 1-boraadamantane **5**^{14a} was predicted to feature a pyramidal arrangement around the tricoordinate boron centre ($\Sigma\alpha = 349.2^\circ$). Jemmis and co-workers investigated unconstrained systems.^{14b} Replacement of the {CH}⁺ fragment of cyclopropylation **6** by the isoelectronic {BH} moiety leads to the perfectly planar borirane **7**. Further replacement of a {CH₂} group of **7** by a {SiH₂} unit yields the BCSi three-membered ring **8**. Notably, the energy minimum **8a** adopts in this case a trigonal pyramidal environment around the boron centre ($\Sigma\alpha = 343.5^\circ$). The conventional structure **8b** featuring a planar boron atom is calculated to be only the transition state for the inversion of **8a** with a barrier of ca 2–4 kcal mol⁻¹ (Scheme 6).

The driving force for the pyramidalization in **8a** has been attributed to the resulting bonding interaction between the boron vacant orbital and the silicon centre. This situation can be schematically depicted by considering a two-electron stabilizing interaction between the in-plane lone pair of a SiH₂ fragment and the out-of-plane boron-centered vacant orbital of a H₂C=BH fragment. Effective overlap between these two orbitals requires



Scheme 6

both the rotation of the SiH₂ fragment and the pyramidalization of the boron centre (Fig. 5).

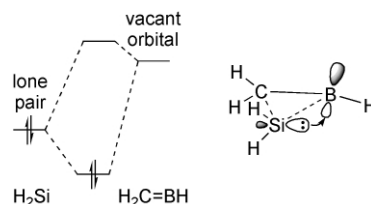
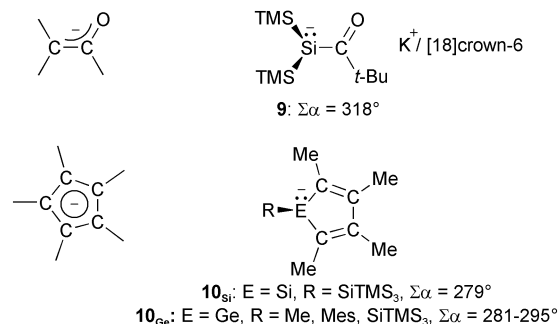


Fig. 5 Schematic representation of the interaction between the silicon lone pair and boron-centered vacant orbital of H₂C=BH.

3.2 Carbanion analogues: trigonal pyramidal versus planar environments

3.2.1 Group 14 analogues: trigonal pyramidal silenolate, silyl, germlyl. It is well known that carbanions adopt trigonal planar geometries when they are included in a π -delocalized system, such as in enolates and cyclopentadienyl anions. In marked contrast, silenolate **9**,¹⁵ silyl and germlyl anions **10_{Si}** and **10_{Ge}**¹⁶ were reported to feature trigonal pyramidal environments around the heavier group 14 element (Scheme 7). As mentioned in the

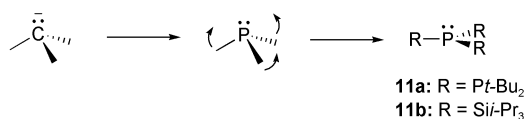


Scheme 7

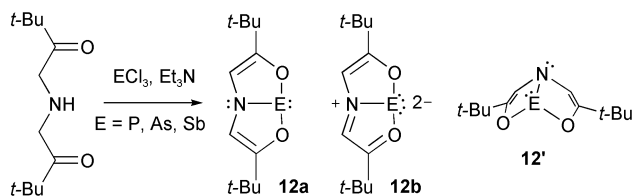
introduction, silicon and germanium have higher planarization energies and form weaker π -bonds than carbon. As a result, the planar delocalized geometries observed for carbon compounds are no longer favoured for the heavier analogues, pyramidal localized structures being preferred.

3.2.2 Group 15 analogues: planar phosphines and phospholes. Phosphines, which are *valence isoelectronic* to carbanions, usually adopt trigonal pyramidal geometries, but with enhanced inversion barriers. Only a few exceptions to this inherent pyramidalization have been reported so far. Indeed, a trigonal planar environment could only be enforced with sterically demanding substituents, as determined structurally for phosphines **11a,b** (Scheme 8).¹⁷

Notably, unusual T-shaped geometries have also been observed by Arduengo *et al.* for derivatives **12** (Scheme 9).^{18,19} X-Ray analyses revealed planar bicyclic structures for all compounds (E = P, As and Sb), with almost linear OEO skeletons [OEO bond angles range from 168° (E = P) to 149° (E = Sb) due to the variation of



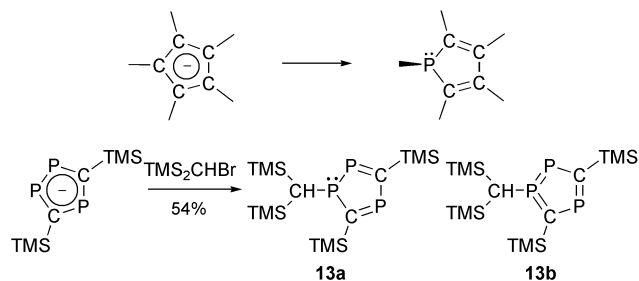
Scheme 8



Scheme 9

the pnictogen size]. The π -delocalized bicyclic framework was demonstrated to be the main factor that enforces the T-shaped geometry over the pyramidal structure **12'**. Moreover, all the geometric data suggest that compounds **12** are best described by structure **12b** rather than **12a**.

The *inert pair effect* of phosphorus is so strong that even 1-phosphacyclopenta-2,4-dienes (phospholes), which are *valence isoelectronic* to cyclopentadienyl anions and thus potentially aromatic, usually adopt pyramidal geometries at phosphorus (Scheme 10).²⁰ In other words, phosphorus planarization generally



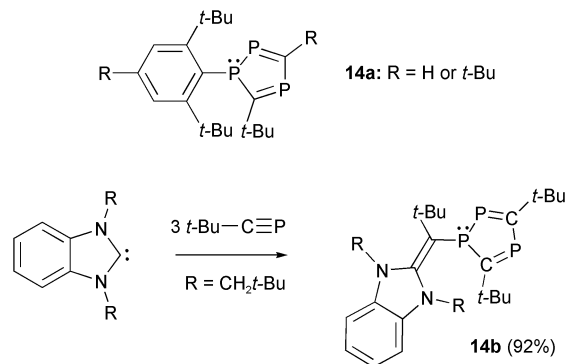
Scheme 10

requires a larger energy than it would receive through aromatic delocalization, and accordingly, phospholes are considered as archetypal non-aromatic systems. So far, this general trend has been challenged only in a few triphospholes. The first delocalized planar structure **13**²¹ was prepared by alkylation of the corresponding triphospholyl anion. The trigonal planar environment around the tricoordinate phosphorus was suggested by NMR in solution, and unambiguously established in the solid-state by an X-ray diffraction study ($\Sigma\alpha = 358.7^\circ$). Moreover, the endocyclic bond lengths indicated significant π -delocalization, in agreement with the contribution of both canonical forms **13a** and **13b**.

The unusual planar geometry of **13** results from a subtle combination of several factors. Firstly, the tricoordinate (σ^3 -P) phosphorus atom has to be substituted by bulky groups, as demonstrated by calculations on model compounds. This steric effect is only effective if bulky substituents are also present at the endocyclic carbon atoms. Secondly, the π -interaction between the σ^3 -P lone pair and diene system is favoured by the introduction of electron-withdrawing substituents such as silyl or boryl groups at the endocyclic carbon atoms. Thirdly, the incorporation of two σ^2 -P atoms in the phosphole framework favours the planar form by increasing the π -conjugation, by decreasing the inversion barrier at the σ^3 -P centre and by opening up the endocyclic C-(σ^3 -P)-P bond angle. The latter effects are brought to the fore for pentaphospholes, for which calculations predict a planar structure even in the parent form P₅H.²²

All these steric and electronic factors are cooperative in **13**, but it might be expected that the number and variety of planar compounds could be extended by employing a subtle combination of these effects. For example, triphospholes **14a** featuring a *t*-Bu

group in the α position to the σ^3 -P centre have been predicted theoretically to retain planar structures (Scheme 11),^{23a} suggesting



Scheme 11

that electron withdrawing substituents are not absolutely necessary at the endocyclic carbon atoms. This hypothesis has been confirmed experimentally with the recent structural characterization of phosphole **14b** resulting from the reaction of an N-heterocyclic carbene with a large excess of phosphalkyne.^{23b}

3.3 Alkene analogues: trigonal pyramidal versus planar environments

Since the seminal work of Lappert and West on distannenes and disilenes, multiple bonding with heavier main group elements has attracted considerable attention, and has been recently comprehensively reviewed.²⁴ As far as geometric considerations are taken into account, *trans*-bent geometries were observed for homo- as well as hetero-nuclear heavier group 14 alkene analogues. These unusual geometries have raised fundamental questions concerning the very nature of this multiple bonding. Schematically, the double bond formation can be described as resulting from two carbenoid fragments, as proposed by Carter, Goddard, Malrieu and Trinquier (CG-MT model).²⁵ Accordingly, the classical σ - π overlaps in alkenes are described by the combination of two triplet carbenes (Fig. 6). For heavier analogues, the double bond is more

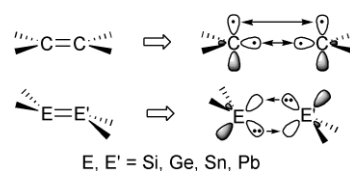
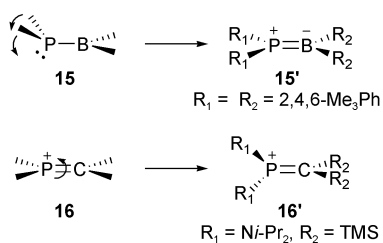


Fig. 6 Schematic representation of the double bond formation from singlet or triplet carbenoid fragments.

appropriately described by the association of two singlet carbenoids (the triplet states are higher in energy mainly due to the *inert pair effect*) via dative, so-called “paw-paw” bonds.²⁶ The resulting bond strength and *trans*-bending have even been quantitatively correlated to the singlet-triplet energy separation of the carbenoids and the σ - and π -bond strengths.

Distorted geometries have also been reported for heteronuclear alkene analogues featuring a phosphorus centre and a group 13 or 14 element. For example, most of the phosphino-boranes were found to adopt a pyramidal geometry at phosphorus (structure **15**), with only negligible overlap between the phosphorus lone pair and the boron vacant orbital (Scheme 12). In other words, the π -bond strength in such compounds is inherently weaker than the energy required for the phosphorus planarization. Nevertheless, suitable steric and electronic manipulation of the phosphorus substituents has been demonstrated to induce classical trigonal planar geometries with enforced π -bonding (structure **15'**). As expected, the presence of a more electron-deficient carbocation in the α position to the phosphorus centre (as in the case of methylene-phosphonium cations²⁷) also induces the planarization of the group 15 element



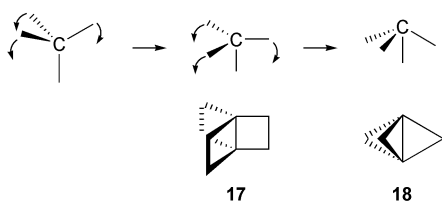
Scheme 12

and thus a classical alkene geometry (structure **16**). However, substituents might induce significant distortions, such as the twist of *ca.* 60° around the P=C double bond reported when amino and silyl substituents are introduced at the phosphorus and carbon atoms, respectively (structure **16'**).

4 Tetracoordinate compounds: alkane analogues

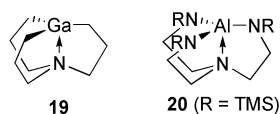
4.1 From tetrahedral to trigonal monopyramidal and inverted geometries

For tetracoordinate carbon compounds, various distortions from the tetrahedral geometry have been reported. Deformation of the conventional arrangement *via* an umbrella motion leads to the trigonal monopyramidal geometry (tmp). Further distortion gives rise to an inverted geometry in which all the four substituents are located in the same hemisphere of space. Ring strain has allowed for the preparation of several derivatives featuring these unusual geometries, the archetypal examples being [2.2.2]propellane **17** and [1.1.1]propellane **18** (Scheme 13).³



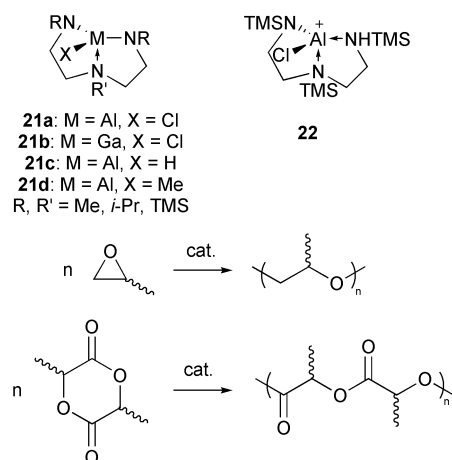
Scheme 13

The trigonal monopyramidal geometry remains very rare for main-group elements. Most of the reported examples concern group 13 or 14 elements and involve intramolecular donor–acceptor interactions. The tmp geometry was first reported in complexes **19** and **20**.²⁸ The relatively rigid tetradentate ligands favours the donor–acceptor interaction, thereby imposing the [3.3.3.0] tricyclic structures.



Bertrand and co-workers extended this tmp geometry to tridentate ligands.²⁹ The neutral group 13 derivatives **21a–d** as well as the cationic aluminium compound **22** were reported to be monomeric and to exhibit distorted tmp geometries (Scheme 14). In all cases, the metallic centre is only slightly displaced from the trigonal plane in the direction of the apical substituent. Due to this tmp coordination, the aluminium centre is accessible for additional ligands, and the aptitude of complexes **21** and **22** to coordinate oxygen-containing substrates has been successfully used for the ring-opening polymerization of heterocycles such as propylene oxide and lactide.

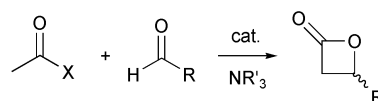
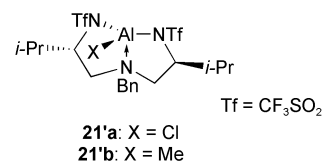
Notably, the tmp geometry has only been observed for polycyclic structures featuring two or three fused five-membered rings. The size of aluminium and gallium atoms (which have very similar radii) appears to make these elements the most favourable at inducing this geometry. Indeed related derivatives featuring the smaller boron atom adopt classical tetrahedral geometries, while



Scheme 14

intermolecular dimerization is usually observed for the larger indium.

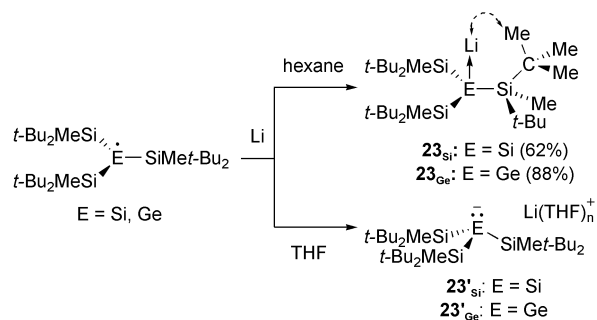
Starting from an L-valine-derived ligand, Nelson *et al.* prepared the related chiral neutral aluminium complexes **21'a,b** (Scheme 15).³⁰ X-ray analysis performed on **21'b** confirmed the expected



Scheme 15

tmp arrangement. Detailed analysis of the structure–activity relationship for the asymmetric acyl halide–aldehyde cyclocondensation demonstrated that the peculiar geometry of these complexes was responsible for their high catalytic activities.

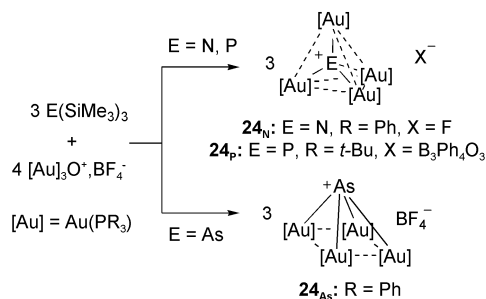
The tmp geometry has also recently been observed for silyl- and germyllithiums **23_{Si}** and **23_{Ge}**, which were obtained in good yields by reduction of the corresponding radicals with lithium (Scheme 16).³¹ The three silyl substituents adopt a trigonal planar arrange-



Scheme 16

ment around the central anionic heavier element, and the lithium counter-cation is coordinated perpendicularly. These unusual tmp geometries observed by X-ray analyses can be attributed to severe steric repulsion between the bulky silyl substituents, hyperconjugation of the anionic centre with adjacent σ*(Si–C) orbitals as well as intramolecular CH₃–Li interactions. The key role of the CH₃–Li agostic interactions in the tmp environment of **23** was demonstrated by the pyramidalized geometries observed for the related ion-pair structures **23'**.

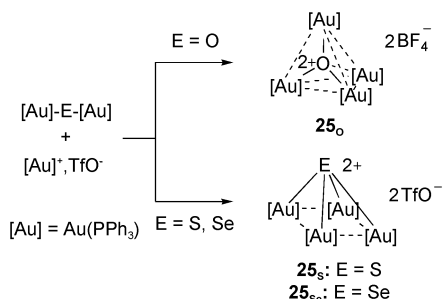
Inverted geometries have also been observed, but only in a few cases, for main group elements. The first example was obtained by Schmidbaur *et al.* when comparing tetra(auro)ammonium salts and their heavier congeners.³² The same synthetic route was used for all group 15 salts, namely the full auration and quaternarization of tris(trimethylsilyl)-amine, -phosphine or -arsine with tris[(phosphine)gold]oxonium tetrafluoroborate (Scheme 17). The tetra-



Scheme 17

(auro)ammonium salt **24_N** adopts a conventional tetrahedral structure with six Au...Au contacts of 3.23–3.34 Å. With a larger central group 15 element such as arsenic, this classical tetrahedral structure would not allow for efficient metal–metal bonding, the so-called “aurophilic interactions”.³³ As a consequence, this structure is abandoned in favour of an inverted geometry, as observed in **24_{As}**. The four gold atoms form in this case a regular arsenic-capped square, with four close Au...Au contacts of *ca.* 2.90 Å. Notably, although the related tetra(auro)phosphonium salts **24_P** were predicted to also adopt a similar inverted geometry,^{32b} they are only stable with large phosphine ligands such as *t*-Bu₃P, which rules out any close approach of the gold atoms and imposes thereby the regular tetrahedral geometry.

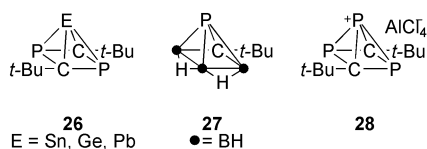
Analogous results were reported with group 16 elements (Scheme 18). Indeed, the oxonium salt(2+) {O[Au(PPh₃)₄]₂ **25_O**



Scheme 18

adopts a conventional tetrahedral structure,^{34a} whereas an inverted geometry is observed for the corresponding sulfonium and selenonium(2+) salts {E[Au(PPh₃)₄]₂ **25_S** (E = S) and **25_{Se}** (E = Se).^{34b,c}

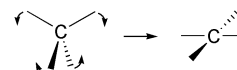
Inverted tetrahedral geometries are also encountered in *nido*-5-vertex clusters.³⁵ This situation has recently been reported for compounds **26–28**, the apical position being occupied by a heavier group 14 element, a neutral and cationic phosphorus centre, respectively.



4.2 From tetrahedral to planar geometry

In 1874, van't Hoff and Le Bel independently recognized that a tetracoordinate carbon atom prefers the tetrahedral geometry,¹ and

thereby paved the way for a profound understanding of stereochemistry. It took almost one century for an alternative geometry, namely planar tetracoordination, to be seriously considered (Scheme 19). The first crystallographically characterized com-



Scheme 19

pound with a planar-tetracoordinate carbon (ptC) atom was reported in the late seventies and since then, this unnatural geometry has stimulated numerous studies, both from a theoretical and preparative point of view.⁴

The planar structure of methane has been predicted to be about 150 kcal mol⁻¹ higher in energy than the corresponding tetrahedral geometry, that is even more than the energy required for C–H cleavage (about 100 kcal mol⁻¹). The peculiar bonding features of ptC can be easily understood from molecular orbital considerations (Fig. 7). The σ-bond system involves the 2s and two of the 2p

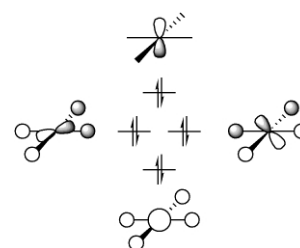
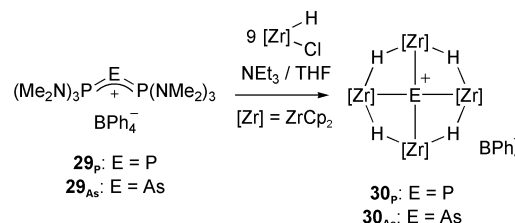


Fig. 7 Schematic representation for the molecular orbitals for planar tetracoordinate carbon.

carbon atomic orbitals, and thus features only six electrons. The remaining 2p_C orbital is perpendicular to the coordination plane and occupied by two electrons.³⁶ Accordingly, it can be expected and it has been indeed established that the ptC geometry is favoured by incorporation into (i) a π-conjugated system (to remove the π lone pair), (ii) small ring systems (from tetrahedral to planar coordination, bond angles are reduced from 109.5° to 90°) or (iii) polycyclic systems (to impose steric constraints). But the most widely used strategy to stabilize ptC relies on substituents functioning both as strong σ-donors and π-acceptors, which thus simultaneously augments the electron density in a σ sense, while removing the energetically unfavourable π-lone pair. This strategy has been verified both theoretically and experimentally. In particular, electropositive boron- and metal-based substituents have proven to be very effective for the stabilization of this so-called “anti-van't Hoff – Le Bel” configuration.

The search for a planar tetracoordination geometry is of course not restricted to carbon compounds and spectacular achievements have indeed been reported for other main-group elements.³⁷ The organometallic phosphonium salt **30_P** has been prepared in low yield by reaction of the triphosphenium salt **29_P** with 9 equivalents of the Schwartz's reagent (Cp₂ZrHCl) in the presence of a large excess of triethylamine as an auxiliary base (Scheme 20).³⁸



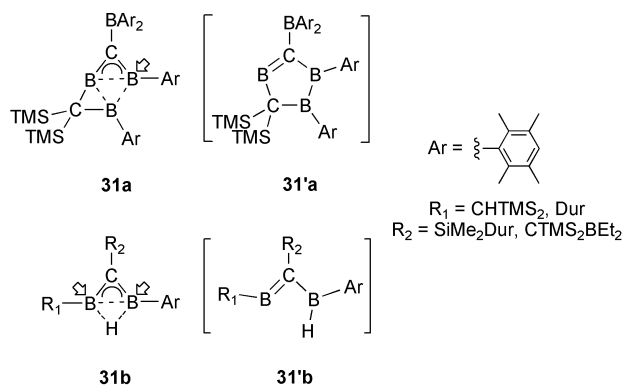
Scheme 20

Surprisingly, the related starting arsenic salt **29_{As}** behaves both as an As and P source leading to a 1:1 mixture of the phosphonium and arsonium salts **30_P** and **30_{As}**. X-Ray diffraction studies revealed the

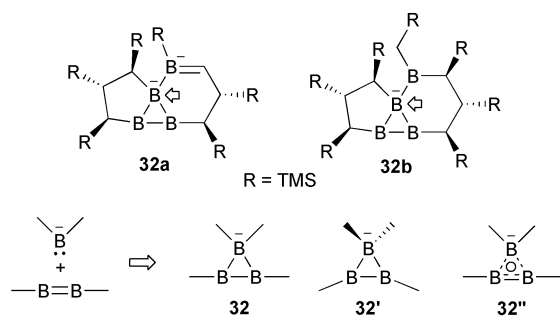
almost ideal square-planar coordination sphere about the central phosphorus and arsenic atoms, with Zr–E–Zr bond angles very close to 90°. Four hydrides bridge adjacent Zr atoms forming a nearly planar eight-membered ring.

According to *ab initio* calculations, the “anti-van’t Hoff – Le Bel” configuration here is 57, 45 and 29 kcal mol⁻¹ more favourable than the tetrahedral configuration for P[Zr(H)Cp₂]₄⁺, As[Zr(H)Cp₂]₄⁺ and the hypothetical Sb[Zr(H)Cp₂]₄⁺, respectively. The main factor giving rise to the planar structure has been attributed to the Zr–E π bonding and the ensuing delocalization of the E lone pair. The steric influence of the ancillary ligands (*i.e.* chelation of the Zr atoms by μ₂-H bridges) does not make a substantial contribution. The influence of the central element E has also been studied computationally for the model compounds E[Zr(H)Cl₂]₄. Notably, all the third row elements (E = Al⁻, Si and P⁺) were predicted to adopt the planar structure, but not the corresponding second row elements (E = B⁻, C and N⁺).

During their investigations on methylene-boranes R–B=C<, Berndt *et al.* obtained non-classical carboranes **31a** and **31b**,³⁹ the first compounds featuring planar tetracoordinate boron atoms (indicated by arrows). These “anti-van’t Hoff – Le Bel” structures do not involve metal centres, but are stabilized in a similar way to **30**, namely through multicentre bonding. This can easily be understood by considering the related classical structures **31'a** and **31'b**: a dashed triangle represents a 3c2e (three-centre two-electron) σ bond and a semi-circle refers to an allylic-type π-system.



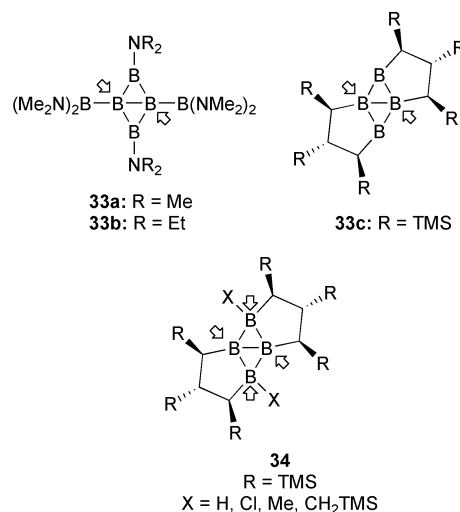
Besides carboranes, planar tetracoordinate boron centres (ptB) have also been observed recently for boranes, such as in triboracyclopropanates **32a,b** (Scheme 21).⁴⁰ Indeed, structural



analyses revealed that the anionic tetracoordinate boron centres of **32a,b** adopt almost planar arrangements. Compounds **32** clearly feature non-classical bonding situations that should be at least schematically depicted if the ptB geometry is to be discussed. For this purpose, triboracyclopropanates **32** will be considered as formally resulting from a carbenoid R₂B⁻ and diborene RB=BR fragments. Accordingly, two situations can be envisaged: (i) a classical structure **32'**, featuring a tetrahedral tetracoordinate boron centre engaged in four 2c2e bonds and (ii) a non-classical case **32''**, featuring a planar tetracoordinate boron centre engaged in a 3c2e

σ bond (represented by a dashed triangle) as well as in a 3c2e π bond (represented by a circle). Structure **32''** combines two of the major stabilizing factors for planar tetracoordinate geometries, namely a π-conjugated system and a small ring. It is thus not surprising that **32''** was predicted to be 55 kcal mol⁻¹ more stable than the classical structure for the parent triboracyclopropanate cyc-B₃H₄⁻.^{40b}

Siebert and Berndt recently reported the synthesis and structural characterization of tetraboranes(4) **33** and tetraboranes(6) **34**,⁴¹ that is compounds featuring a B₄ ring with 4 and 6 substituents, respectively. All of these compounds adopt diamond-shape structures and feature planar tetracoordinate boron centres (indicated by arrows). Detailed investigations of the bonding situation in these tetraboranes revealed in both cases the presence of a 4c2e π system. The delocalization of these 2π electrons is only possible when the corresponding 2p_B orbitals are perpendicular to the B₄ rings, and this is therefore the major factor for the ptB geometries observed in these compounds.



5 Conclusions

The specific properties of group 13 to 15 heteroelements have allowed for the synthesis and structural characterization of numerous distorted compounds over the last twenty five years, as highlighted here. Combined with the synthesis of stable versions of highly reactive carbon moieties (such as carbenes,^{42a} radicals^{42b} and diradicals,^{42c} anti-aromatic systems^{42d}...), these studies obviously contribute to a better understanding of chemical bonding and clearly open up new areas of research (such as *bent*-multiple bonds and odd-electron bonds...). Besides this structural and fundamental interest, unusual geometries have often been associated with peculiar behaviour. The most representative example certainly concerns trigonal monopyramidal group 13 derivatives, which have found practical applications due to their enhanced Lewis acidities.

Group 13 to 15 elements allow for many combinations, and it can thus be reasonably envisioned that numerous other distorted derivatives will be discovered in the future.

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