

Main-group elements as transition metals

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The last quarter of the twentieth century and the beginning decade of the twenty-first witnessed spectacular discoveries in the chemistry of the heavier main-group elements. The new compounds that were synthesized highlighted the fundamental differences between their electronic properties and those of the lighter elements to a degree that was not previously apparent. This has led to new structural and bonding insights as well as a gradually increasing realization that the chemistry of the heavier main-group elements more resembles that of transition-metal complexes than that of their lighter main-group congeners. The similarity is underlined by recent work, which has shown that many of the new compounds react with small molecules such as H₂, NH₃, C₂H₄ or CO under mild conditions and display potential for applications in catalysis.

Heavier main-group elements have fundamentally different electronic properties from their lighter congeners. Until the last two decades of the twentieth century, these differences were often masked by similarities in the stoichiometry, structure and chemical behaviour of the known compounds. Commonly held perceptions of the main-group and transition compounds as well as their chemistries may be summarized by a partial list of their properties, shown in Table 1.

These generalizations provide a basis for the view that the chemistry of the transition metals is inherently richer than that of the main-group elements. Of course, exceptions can be found for many of the points listed. However, numerous recent discoveries have shown how several types of main-group compounds can behave like transition-metal complexes, so that many of the generalizations are now invalid. The discoveries that led to this change originated from a simple desire to synthesize main-group compounds that were unknown as stable species. These featured one or more of the following: (1) multiple bonds between heavier main-group elements such as Al, Si, P or their heavier congeners¹; (2) stable low-valent derivatives with open coordination sites^{2–4}; (3) molecules with quasi-open coordination sites as a result of frustrated Lewis pairs⁵; (4) stable paramagnetic electron configurations (that is, radicals) with unpaired electrons centred on heavier main-group elements^{6–8}; or (5) stable singlet diradicaloid electron configurations⁹. Not only were such compounds unknown, but it was also assumed in many cases that they were incapable of a stable existence^{10,11}.

At present, dozens of stable compounds from the above classes have been isolated and they can no longer be regarded as curiosities.

However, much of the discussion of the bonding of the heavier main-group element compounds (especially multiple bonded species) has been dominated by comparisons with their lighter element congeners, such as alkenes and alkynes. The common characteristic of the new species is that they all possess frontier orbitals with small energy separations; this is a feature more often associated with transition-metal complexes. As a result, many of them display a reactivity¹² towards small molecules such as H₂, NH₃ or C₂H₄ that until recently had been known only for transition-metal species. The time is therefore ripe for a comparison of heavy main-group compounds with transition-metal complexes, and so a discussion of their similarities is the major theme of this review.

Bonding in the heavier main-group elements

The most fundamental difference^{13,14} between the light (for example, B, C, N or O) and heavy main-group elements is the large jump (~50%) in the covalent radii between the first and second rows of the periodic table (for example, C (0.77 Å), Si (1.17 Å)¹⁵, which is due to their different core electronic structures¹³. This large size increase permits the higher coordination numbers observed in compounds such as [Al(OH₂)₆]³⁺, [SiF₆]^{2–} or PCl₅. However, none of these display the coordinative or oxidative flexibility characteristic of complexes of the transition metals. Furthermore, they generally do not undergo simple reactions, such as insertions and oxidative additions/reductive eliminations, found in catalytic cycles mediated by transition-metal complexes. The lack of molecules displaying such reactivity was due to a general absence of main-group compounds that had open coordination sites and valence orbitals separated by modest energies (≤4 eV) that are characteristic of many transition-metal species. However, this deficiency has been gradually remedied over the past three decades by many research groups who often pursued quite a different goal—the preparation of stable compounds having multiple bonding between two heavier main-group elements.

The key to their isolation lay in the recognition that the heavier main-group elements were indeed much larger than the lighter elements and therefore required very large substituents to prevent association of multiple bonded species into oligomers or polymers. Exactly how large the groups had to be was not recognized until the 1970s, when Lappert used the very bulky alkyl group –CH(SiMe₃)₂ to prepare a Sn analogue of an alkene, R₂SnSnR₂ (R = CH(SiMe₃)₂) (ref. 16; Me, CH₃). The original intention was to prepare the first stable monomeric group 14 element dialkyls :MR₂ (M = Ge, Sn or Pb; R = CH(SiMe₃)₂), which are heavier element analogues of carbenes. But when the

Table 1 | Current views of main-group and transition-metal compounds

Transition-metal compounds	Main-group compounds
Usually have partially occupied valence <i>d</i> orbitals that are often relatively close in energy.	The valence <i>s</i> or <i>p</i> orbitals are either fully occupied or empty and are far apart energetically.
Often coloured as a consequence of small orbital energy separations.	Usually colourless.
Often interact with small molecules such as CO, C ₂ H ₄ or H ₂ .	Generally do not interact strongly with CO, C ₂ H ₄ or H ₂ .
Often paramagnetic.	Usually diamagnetic.
Stereochemical electron pair character less pronounced.	Have stereochemically active electron pairs which form the basis of VSEPR theory.
Antiferromagnetic coupling is common.	Antiferromagnetic coupling in stable compounds not common.

VSEPR, valence shell electron pair repulsion.

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structures of the highly coloured :MR_2 species were determined in the solid state^{17,18} they were found to be metal–metal bonded dimers, that is, Ge or Sn analogues of ethylene, whose most striking feature was the pyramidal coordination of the Ge or Sn atoms (Fig. 1a).

The Ge–Ge and Sn–Sn distances (2.347(2) and 2.768(1) Å, respectively) were just slightly shorter than normal single-bond lengths such as those in elemental Ge (2.44 Å) or Sn (2.80 Å)¹⁵. The distances were misleading, however, because the dimeric structures were found to dissociate to monomeric $\text{:Ge}\{\text{CH}(\text{SiMe}_3)_2\}_2$ or $\text{:Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ units in solution¹⁶. The bonds were originally represented by Lappert as shown in Fig. 1, where the Ge or Sn atoms were linked by either two weak donor–acceptor bonds (Fig. 1b) or by a single bond with a resonating lone pair (Fig. 1c). The original Ge and Sn species were later joined by Si and Pb analogues. In the lead compound $\text{:Pb}\{\text{CH}(\text{SiMe}_3)_2\}_2$ the Pb–Pb distance (4.129 Å) is so long that it scarcely merits consideration as a bond¹⁹. West's synthesis of the landmark disilene $\text{Mes}_2\text{Si}=\text{SiMe}_2$ (Mes = mesityl, that is, $\text{C}_6\text{H}_2\text{-2,4,6-Me}_3$)²⁰ showed that it had an almost planar core structure like that of ethylene and a short Si=Si bond of ~ 2.16 Å (compare 2.34 Å for an Si–Si bond). Thus, on proceeding down the group, the original σ and π C=C bond is mostly transformed into two non-bonded lone pairs at the heaviest element, lead. Both bonding representations in Fig. 1c are characterized by the simultaneous existence of partial unsaturation and electron richness at the metals. It can be seen that in each of the resonance forms there is an electron pair (donor) at one metal whereas the other metal in the structure carries a positive charge and is electron deficient. Furthermore, each resonance form is 'missing' a bond, according to the normal rules of valence. For this reason they are regarded as non-Kekulé structures. Heavier group 14 element alkyne analogues display similar behaviour, as shown in Table 2^{21–24}.

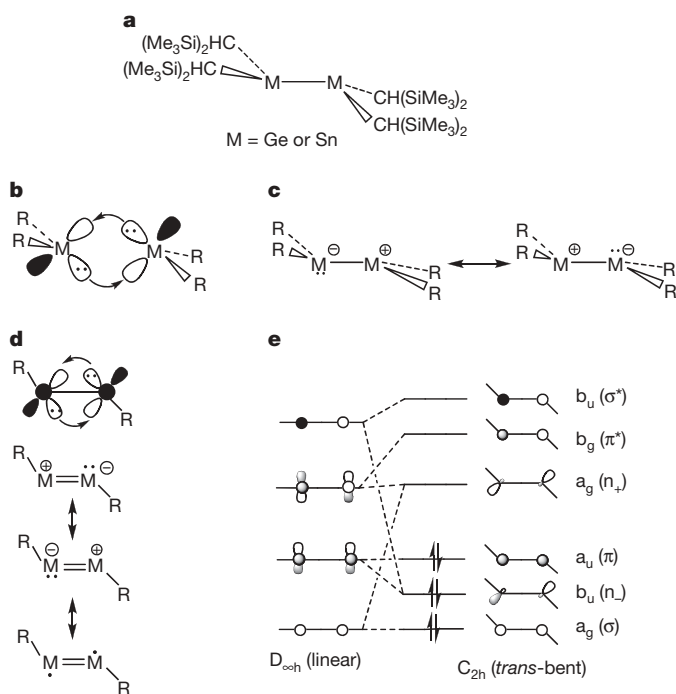


Figure 1 | Bonding in group 14 analogues of ethylene and alkynes. **a**, The *trans*-pyramidal structure of R_2MMR_2 (M = Ge or Sn). **b**, **c**, Simple bonding models for the non-classical double bond in R_2MMR_2 (M = Si, Ge, Sn, Pb). **d**, Valence bond models for bonding in moderately *trans*-bent, heavier group 14 alkyne analogues. **e**, In the molecular orbital description of bonding in group 14 alkyne analogues, second order Jahn–Teller mixing (right) of σ^* and π^* as well as σ and π^* levels (n_+ and n_- signify a non-bonding orbital which is symmetric or unsymmetric with respect to inversion) leads to non-bonded electron pair character (as in the $b_u(n_-)$ orbital) at the heavier group 14 elements.

Here the triple bond in the linear acetylene fades to a single one at lead where the electrons in the two original π -bonds are converted into two non-bonded electron pairs. Again, the amount of geometrical distortion (that is, bending) increases as the group is descended, and it is possible to write these distorted structures using a valence-bond approach (Fig. 1d), analogous to Lappert's representations of the ethylene analogues (Fig. 1b and c). In essence, the heavier alkyne analogues also contain an increasing degree of non-bonded electron localization at the heavier element while having, at the same time, electron deficient, unsaturated character because of incomplete electron sharing in the multiple bond (each of the structures drawn on the left side of Table 2 is non-Kekulé to some degree). In this way, both donor and acceptor sites within the molecule are created. As will be seen in the next section, this is the key to their reactivity.

The molecular orbital (MO) treatment of the bonding in heavier group 14 element alkyne analogues also affords valuable insights (Fig. 1e). In this approach, the geometrical distortions are explained on the basis of mixing of anti-bonding and bonding levels within the molecule. This mixing is a second order Jahn–Teller effect^{25–28}, which arises from a symmetry allowed, intramolecular mixing of an unoccupied non-bonding or anti-bonding orbital with a bonding orbital (generally the HOMO (highest occupied molecular orbital) in multiple bonded species)^{28,29}. The orbital mixing introduces non-bonding, lone pair character in a HOMO (generally a π -orbital) which can have a drastic effect on molecular shape. The extent of the mixing is inversely proportional to the energy separation of the orbitals and is maximized in the heavier elements, because the weakened bonding often permits a close approach (< 4 eV) of the molecular levels. Other approaches to the distorted geometries in the multiple bonded heavier main-group molecules have also been developed, but because of space restrictions are not discussed here^{30–32}.

Second order Jahn–Teller mixing of a σ^* - and an in-plane π -orbital in the heavier group 14 alkyne analogues occurs on bending as both orbitals have b_u symmetry in the C_{2h} point group^{28,29}. This converts the original, in-plane π -orbital into an approximately non-bonded lone pair n_- combination (sometimes called a slipped π -bond). Mixing of the σ - and π^* -orbitals (both a_g symmetry) also occurs, which weakens the σ -bond. In the *trans*-bent (C_{2h}) structure, the HOMO (π -orbital, a_u) can act as a Lewis base electron donor, whereas the virtual lone pair combination $a_g(n_+)$ can act as a lone-pair acceptor orbital. Although it is based on different assumptions, the MO explanation of these donor and acceptor sites (Fig. 1e) is consistent with the analogous valence bond drawings (Fig. 1d).

Similar considerations apply to neighbouring group 13 element derivatives. The much discussed, formally $\text{Ga}\equiv\text{Ga}$ bonded red salt $\text{Na}_2\text{Ar}^*\text{GaGaAr}^*$ (ref. 33) of Robinson contains the dianion $[\text{Ar}^*\text{GaGaAr}^*]^{2-}$, which is analogous to $\text{Ar}^*\text{GeGeAr}^*$ and has a

Table 2 | Structural data for heavier group 14 element alkyne analogues

Compound	M=M (Å)	M=M–C bending angle (degrees)	Shortening* (%)
$\text{R-Si}\equiv\text{Si-R}$	2.0622(9) (ref. 21)	137.44(4)	11.87
$\text{Ar'-Ge}\equiv\text{Ge-Ar'}$	2.285(6) (ref. 22)†	128.67(8)	6.35
$\text{Ar'-Sn}\equiv\text{Sn-Ar'}$	2.6675(4) (ref. 23) †	125.1(2)	5.07
$\text{Ar}^*\text{-Pb}\equiv\text{Pb-Ar}^*$	3.1811 (ref. 24)‡	94.26(4)	–9.69

* Shortening with respect to a single bond.

† $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2$.

‡ $\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3)_2$.

trans-bent structure (Ar^* , $\text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3)_2$; $i\text{-Pr}$, $\text{CH}(\text{CH}_3)_2$). Also, there are formally double-bonded species such as the green $\text{Ar}'\text{GaGaAr}'$, which dissociates in solution to $:\text{GaAr}'$ monomers, which have donor and acceptor sites³⁴ (Ar' , $\text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,6-}i\text{-Pr}_2)_2$). In contrast, the heavier group 15 element multiple bonded compounds, exemplified by Yoshifuji's landmark diphosphene $\text{Mes}^*\ddot{\text{P}}=\ddot{\text{P}}\text{Mes}^*$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{-2,4,6-}t\text{-Bu}_3$) (ref. 35; $t\text{-Bu}$, $\text{C}(\text{CH}_3)_3$), have a conventional double bond with σ - and π -components due to p -orbital overlaps and lone pairs that are mainly s in character. These compounds have no non-Kekulé character, and their chemistry more resembles that of unsaturated organic compounds. The heaviest element derivatives $\text{RM}=\text{MR}$ ($\text{M} = \text{Sb}$ or Bi) have bond shortenings of 8–9%, which show that π -bonding is maintained in the higher rows of the p -block elements³⁶.

Reactivity of heavier main-group compounds

Reactions with saturated small molecules. In the previous section, it was argued that the multiple bonded heavier main-group compounds resemble transition-metal complexes owing to the presence of occupied and unoccupied frontier orbitals that are energetically accessible. How is this reflected in the chemistry of the main-group species? In organotransition-metal chemistry, the most important or basic reaction types are oxidative additions, reductive eliminations and insertions. Most steps in homogenous catalytic cycles involve one or more of these reactions—usually with small molecules, such as hydrogen, olefins, carbon monoxide, ammonia and related molecules—under mild conditions. Until recently, no comparable reactions with main-group molecules were known. However, many such reactions have been recently discovered for the multiple bonded/unsaturated main-group compounds.

The simplest of these reactions involve the addition of an H_2 molecule, which is analogous to a key step in many homogeneous transition-metal catalytic cycles such as olefin, alkyne or arene hydrogenation and hydroformylation. In several instances, the addition is reversible and, in a defining event in the development of coordination chemistry, Kubas showed that it was even possible to isolate transition-metal complexes of H_2 itself, which represent the initial stage of an oxidative addition reaction³⁷. Until recently, no H_2 additions were known for main-group compounds under mild conditions. However, in 2005 it was shown that the Ge alkyne analogue $\text{Ar}'\text{GeGeAr}'$ reacted directly with H_2 under ambient conditions to give the hydrogenated products $\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$, $\text{Ar}'(\text{H})_2\text{GeGe}(\text{H})_2\text{Ar}'$ and $\text{Ge}(\text{H})_3\text{Ar}'$; these were all structurally characterized by X-ray crystallography³⁸. Calculations indicate that in this reaction and that of its Sn analogue $\text{Ar}'\text{SnSnAr}'$ (which reacts to give $\text{Ar}'\text{Sn}(\mu\text{-H})_2\text{SnAr}'$ exclusively) the initial step involves a synergic interaction of frontier orbitals with H_2 (Fig. 2)³⁹.

The interaction involves donation from the σ -orbital of H_2 into the LUMO of $\text{Ar}'\text{GeGeAr}'$, which is a symmetric unoccupied n_+ non-bonding combination (compare Fig. 1e). There is a synergic electron donation from the π -HOMO orbital of the germanium species into the σ^* -orbital of H_2 . This weakens the H–H bond sufficiently to enable oxidative addition to occur. Clearly, the mechanism whereby H_2 is activated by the main-group and transition-metal compounds is analogous in the symmetry of the frontier orbitals

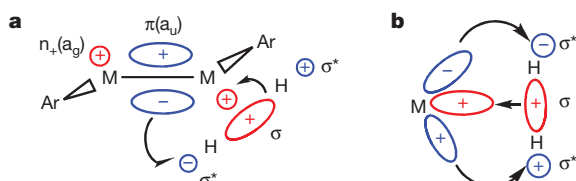


Figure 2 | Similarity of H_2 interactions with main-group and transition-metal compounds. **a**, The initial interaction of H_2 with the π (HOMO) and n_+ (LUMO) frontier orbitals of ArMMAr ($\text{M} = \text{Ge}$ or Sn ; $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_2)_2$), which lie only ~ 2 eV apart. This is comparable to **b**, the interaction of H_2 with the frontier d orbitals in a transition-metal complex (M is a transition metal).

and their energy separations. The main difference lies in the orbital labels. This type of activation by main-group species is general, as shown by the fact that several other unsaturated heavier main-group molecules, including the carbene-like $:\text{GeAr}_2$ and $:\text{SnAr}_2$ as well as the monovalent $:\text{GaAr}$ species, have been recently shown to react directly with H_2 (Fig. 3a and b)^{39,40}.

Bertrand and his group showed in 2007 that the reaction of the related stable carbenes such as $:\text{C}(t\text{-Bu})\text{Ni-Pr}_2$ with H_2 (Fig. 3c) affords the addition product $\text{H}_2\text{C}(t\text{-Bu})\text{Ni-Pr}_2$ (ref. 41), in contrast to the reaction with the heavier tin carbene analogue (Fig. 3a), which leads to arene elimination ($i\text{-Pr}$, $\text{CH}(\text{CH}_3)_2$). All of the products were characterized spectroscopically and by X-ray crystallography.

In another major advance, Stephan and co-workers showed that H_2 can be bound in a reversible manner by the use of a Lewis-acid–base strategy, termed ‘frustrated Lewis pairs’, and incorporated in phosphine boranes (Fig. 3d)⁴². The important feature of the reaction is the steric prevention of the formation of a stable Lewis acid–base phosphine–borane adduct by the large phosphine substituents (hence the term frustrated Lewis pair) while permitting the synergic interaction of the empty borane $2p$ orbital and the phosphine lone pair orbital with the H_2 molecule. In effect, there is an available unfilled acceptor orbital (on boron) and a donor orbital (phosphorus electron pair) that can fulfil a similar function to the frontier orbitals on transition metals and unsaturated, multiple bonded main-group compounds. The initial step is very likely to be the side-on reaction of the σ -bond of H_2 with the borane, with population of the H_2 σ^* -orbital by electron density from the phosphine. In other words, the activation of H_2 proceeds by a similar initial orbital interaction to those described above, although the ultimate disposition of H_2 differs in that it is polar- H^+ at phosphorus and H^- at boron. Mild heating of the resulting phosphonium borate releases H_2 to regenerate the phosphine and borane. Recent work has extended the list of H_2 frustrated Lewis pair activation systems to include borane complexes of carbenes^{43,44}, amines⁴⁵ and phosphines^{46,47}. It seems very likely that other combinations of donor/acceptor species derived from various main-group elements will also be developed.

In addition to the activation of H_2 , Bertrand and co-workers also showed that carbenes react with NH_3 at -78°C to afford N–H activation products (Fig. 3e)⁴¹. This was the first instance of the insertion of a main-group element into the N–H bond of ammonia under mild, uncatalysed conditions. The heavier germanium and tin carbene analogues $:\text{GeAr}_2$ and $:\text{SnAr}_2$ as well as the gallium species $:\text{GaAr}$ were also shown insert into N–H bonds below room temperature^{40,48}. These reactions parallel those in transition metals where, for

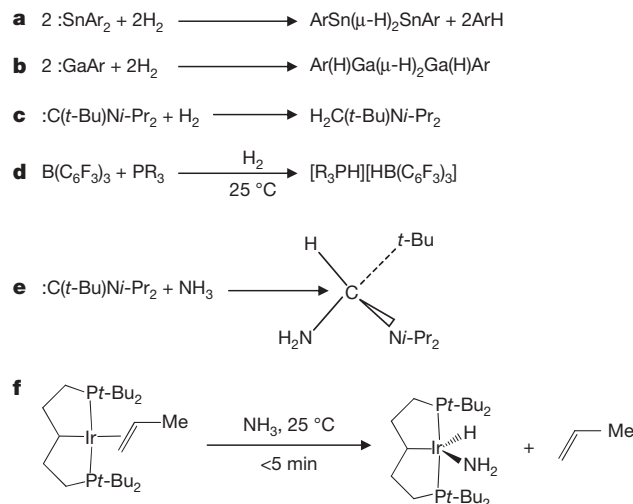


Figure 3 | The reactions of various main-group and transition-metal species with H_2 or NH_3 . $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$ or $\text{C}_6\text{H}_3\text{-2,6-}(\text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_2)_2$.

example, it has been demonstrated that iridium complexes can insert the iridium metal into N–H bonds (Fig. 3f)⁴⁹. Such insertions are of high current interest because it is believed that they are likely to be an important step in the addition of ammonia or other amines to unsaturated molecules, such as olefins.

Activation of unsaturated molecules. The complexation and activation of unsaturated molecules under mild conditions by various main-group species, previously the province of transition-metal complexes, is also an emerging feature of the current literature. For example, many of the multiple bonded species mentioned in the previous section react directly with numerous alkenes and alkynes to give cyclized or addition products^{50–52}. In addition, Stephan and co-workers have shown that the $Pt-Bu_3/B(C_6F_5)_3$ system reacts cleanly with ethylene to form the zwitterionic salt $t-Bu_3P^+CH_2CH_2B^-(C_6F_5)_3$ (ref. 53). However, the reversible reaction of alkenes with main-group compounds is much rarer. It had been shown a number of years ago that $:Sn\{CH(SiMe_3)_2\}_2$ reacted reversibly with a strained alkyne to afford a stannacyclopentene⁵⁴. However, more recent investigations⁵⁵ have shown that the deep green distannylene $Ar'SnSnAr'$ reacts reversibly with ethylene at room temperature and one atmosphere pressure to yield the double cycloadduct $Ar'Sn(\mu_2:\eta^1:\eta^1-C_2H_4)_2SnAr'$, which was shown to have a 1,4-distannabicyclo[2.2.0] butane structure by X-ray crystallography (Fig. 4a). The association is moderately favoured and has a reaction enthalpy of $-48(4) \text{ kJ mol}^{-1}$. Finely balanced electronic and steric factors control the energetics of the reaction and calculations show that the initial step involves a synergic interaction between the frontier orbitals (Fig. 4b). These interactions have an obvious parallel with the Dewar-Chatt model for the corresponding interactions in Zeise's salt⁵⁶ (Fig. 4c).

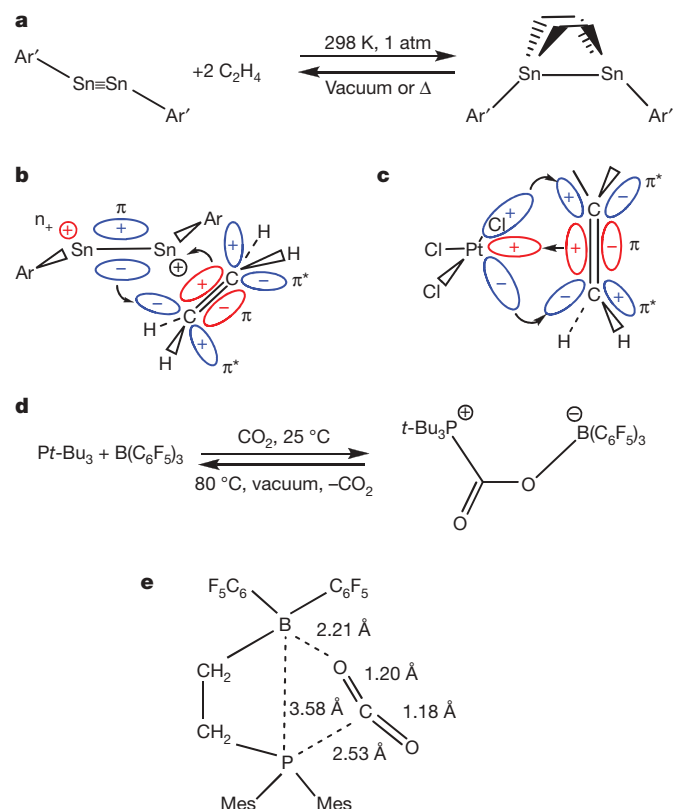


Figure 4 | Reversible reactions of main-group compounds with unsaturated molecules. **a**, The reaction of ethylene with $Ar'SnSnAr'$ (ref. 55). $Ar' = C_6H_3-2,6(C_6H_3-2,6-i-Pr)_2$ or $C_6H-2,6(C_6H-2,4,6-i-Pr)_2-3,5-i-Pr_2$. Orbital interactions between ethylene and the distannylene (**b**) are comparable to those between platinum d orbitals and ethylene in Zeise's salt (**c**). **d**, Reversible complexation of CO_2 by $Pt-Bu_3/B(C_6F_5)_3$. **e**, The transition state of the reaction between CO_2 and $Mes_2PCH_2CH_2B(C_6F_5)_3$ (ref. 58).

The phosphine–borane frustrated Lewis pair system has also been shown to react with several olefins and alkynes and other unsaturated molecules such as N_2O (ref. 57). In addition, a remarkable reversibility has been demonstrated for the reaction with CO_2 (Fig. 4d). The tethered 1,2-phosphine–borane $Mes_2PCH_2CH_2B(C_6F_5)_2$ also complexes CO_2 reversibly under ambient conditions⁵⁸. The structures of both of the CO_2 adducts were determined by X-ray crystallography, and the mechanism of the reaction with CO_2 was probed by density functional theory (DFT) computations. In the transition state, the CO_2 displaces the weak phosphorus–boron bond and becomes associated via a donor interaction of one of the oxygens to the boron atom, while there is corresponding acceptor interaction between the CO_2 carbon and the phosphorus lone pair (Fig. 4e). This mode of activation typically illustrates the parallel between the synergic interactions of the frontier orbitals of transition metals and main-group atoms. The development of homogeneous main-group catalysts is also an area of intense current interest. At present, most of this work is based on the phosphine–borane frustrated Lewis pair systems. Stephan and his group have shown that phosphonium–borate salts $(R_2PH)(C_6F_4)BH(C_6F_5)_2$ ($R = Mes$ or $t-Bu$) catalyse the addition of hydrogen to imines or nitriles, as shown in Fig. 5 (ref. 59).

In addition, Erker and co-workers showed that the tethered phosphineborane $Mes_2PCH_2CH_2B(C_6F_5)_2$ catalyses the addition of H_2 to imines or enamines, for example, $t-BuN=C(H)Ph$ or $H_2C=C(Ph)(piperazino)$, under mild conditions⁶⁰. This cycle bears a strong resemblance to corresponding catalytic cycles involving transition metals in their major features.

Stable radicals and diradicaloids

Numerous stable radicals with unpaired electrons localized on O, N or S atoms (or combinations of them) have been known for many years, in some cases since the nineteenth century. The first persistent radicals, whose unpaired electron was undelocalized and centred primarily on a heavier main-group metal, resulted from the photolysis of solutions of $:Sn\{CH(SiMe_3)_2\}_2$. This afforded, via disproportionation, an EPR (electron paramagnetic resonance) signal corresponding to the radical $\cdot Sn\{CH(SiMe_3)_2\}_3$ which persisted in solution for several months⁶¹. The EPR spectrum showed that it had pyramidal coordination at the tin, in contrast to the generally planar geometries in carbon centred radicals. Other related persistent radicals of germanium and tin with alkyl or amido substituents were also obtained⁶. Similarly, persistent phosphino and arsino radicals could be synthesized⁶². Later, beginning in the 1990s, several stable heavier main-group element radicals were crystallized and their structures were determined by X-ray crystallography^{6,8}. The stable undelocalized radicals of the heavier main-group elements correspond to

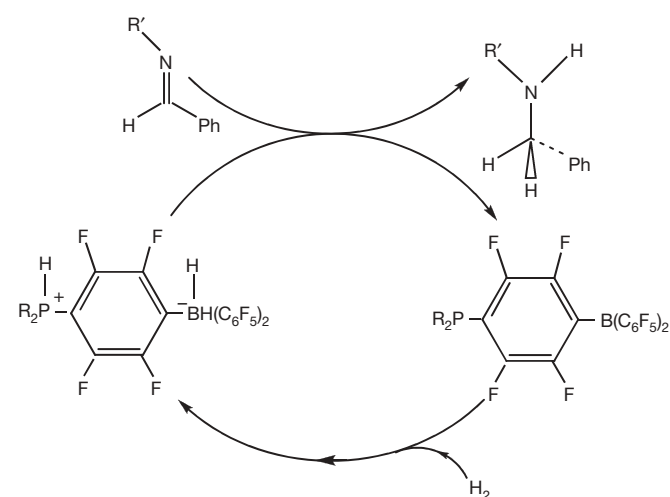


Figure 5 | Catalytic cycle for the reduction of imines by phosphine-boranes. $R = 2,4,6-Me_3C_5H_2$ or $t-Bu$; $R' = t-Bu$, benzyl, $CHPh_2$, SO_2Ph . From ref. 59.

transition-metal paramagnetic molecules. However, the main-group radicals, where the electron is localized on one atom, differ from the analogous magnetic transition-metal species in that there is generally just a single unpaired electron in a non-degenerate orbital, whereas in the transition-metal complexes (especially those of the first row), there can be as many as five unpaired electrons in five degenerate orbitals.

An important development in the late 1980s and 1990s was the synthesis of a wide range of novel diradicaloids whose common feature is the incorporation of main-group elements, such as boron, nitrogen, silicon, phosphorus or sulphur, in their structures⁹. They are related to diradicals—organic molecules which have two unpaired electrons of opposite spin in two, almost degenerate, non-bonding molecular orbitals. However, if some or all the carbon atoms in the skeletons of the organic diradicals are replaced by main-group elements, stable analogues of the organic diradicals can be isolated in certain cases. These isolable compounds are generally referred to as diradicaloids (or biradicaloids). The distinction from diradicals comes from the fact that, in order to make them isolable, some degree of coupling of the unpaired electrons must be accepted. This inevitably diminishes their diradical character and, in fact, all diradicaloids isolated so far are (formally, at least) closed shell species. The inclusion of heavier main-group elements as part of the diradicaloid skeleton provides the electronic and structural flexibility for this to occur. They include compounds that are based on sulphur-nitrogen^{7,63}, phosphorus-carbon⁶⁴ and boron-phosphorus⁶⁵ systems, as well as group 14 element rings and cages⁶⁶. They feature two relatively weakly coupled electrons in an orbital localized on two separate atoms such that the molecules can be written as if they lack a bond (non-Kekulé structures; Fig. 6a–c).

The key to their isolation involves the fact that certain bonds within the structures can be lengthened considerably without completely breaking them. When this occurs, there is substantial localization of an electron on each atom while at the same time these electrons are relatively weakly coupled because of the bond stretching (broken lines in Fig. 6a–c)⁹. They can be considered as strongly anti-ferromagnetically coupled main-group species, with interaction energies corresponding to wavenumbers of several thousand cm^{-1} , which are loosely related to antiferromagnetically coupled transition-metal centres. This analogy is represented in Fig. 6d and e. The reaction of the β -diketiminate cobalt complex (η^6 -toluene)Co

[NNMe₂] with an arylazide or nitrosoarene cleaves an N–N or N–O bond to afford the respective bridged products (Fig. 6d)⁶⁷. Similarly, Ar'GeGeAr' reacts with the azide N₃SiMe₃ or a nitrosoarene to afford diradicaloid products^{68,69} that have analogous core structures to the bridged cobalt species (Fig. 6e). It is noteworthy that both the germanium and cobalt complexes are capable of four electron reductions of nitrosoarenes to give products with broadly similar structures.

There have been numerous quantum mechanical calculations on the main-group diradicaloid systems^{70–72}. In the boron-phosphorus diradicaloids (Fig. 6b), the coupling of the 'unpaired' boron electrons across the B₂P₂ ring results in a lifting of the initial degeneracy of the two singly occupied boron *p* orbitals to afford a doubly occupied π -bonding HOMO and an unoccupied π^* anti-bonding LUMO. The computations show that the extent of diradical character is strongly correlated to the substituents at boron and phosphorus. The calculated singlet–triplet energy separations and LUMO occupancy, which are indicators of diradical character, vary quite considerably. Thus, LUMO occupation numbers (e^-) as high as 0.39 e^- and singlet–triplet gaps as low as 5.8 kcal mol^{−1} have been calculated. Bertrand and his group have synthesized a series of such compounds, and shown that the B–B separation can be varied from 1.83 to 2.57 Å (a 40% bond stretching) by changing the R and R' substituents. In addition, the *i*-Pr₂P(μ -BPh)₂Pi-Pr₂ ring species displays a temperature dependent equilibrium in solution between a purple-coloured diradicaloid isomer with a very long B–B distance of 2.57 Å and a colourless isomer with a normal B–B single bond of 1.86 Å (ref. 70). The chemistry of the cyclic B–P systems, such as their ready abstraction of chlorine from CDCl₃ and the addition of Me₃SnH to the boron atoms, is consistent with their diradical character⁷³. Finally, it is noteworthy that calculations⁷⁴ on models of the heavier group 14 element dimetallenes (Fig. 1a) and dimetallynes (Table 2) have shown them to have varying degrees of diradical character (the Si, Ge and Sn species in Table 2 are also non-Kekulé molecules, as they are 'missing' a bond, compare Fig. 1b), which is consistent with their high reactivity.

Conclusion and outlook

Until recently, the synthesis of stable compounds with multiple bonds between heavier main-group elements was inspired almost exclusively by their relationship to multiple bonded organic compounds.

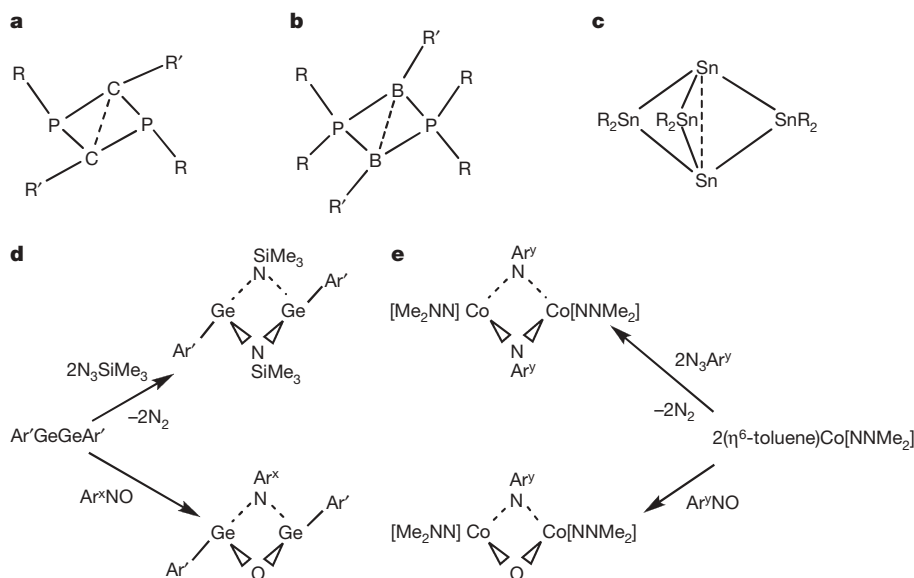


Figure 6 | Structures and reactions of main-group diradicaloids. **a–c**, Illustration of three different stable main-group diradicaloids. Interactions between the radical centres are represented by dotted lines. (R and R' are a variety of bulky alkyl, aryl groups) **d, e**, Parallel molecular

structures resulting from the treatment of a main-group compound^{68,69} (**d**) and a transition-metal species⁶⁷ (**e**) with azides and nitrosoarenes. Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*-Pr₂)₂; Ar^x = C₆H₃-2-Me; Ar^y = C₆H₃-3,5-Me₂; [NNMe₂] = HC{C(Me)N(C₆H₃-2,6-*i*-Pr₂)₂}₂.

Moreover, their bonding was judged on the basis of the well tried and tested models used for organic species. However, it gradually became clear that the simple bonding models used for the lighter organic derivatives were inadequate to deal with their heavier main-group element congeners. Weaker bonding (both σ and π) and diminished hybridization led to the appearance of non-bonded electron density and concomitant geometrical distortions. These could be explained on the basis of a second order Jahn–Teller effect, which can occur because of the lower separation of the molecular energy levels.

However, it was the recently discovered ability of many heavier species to display previously unknown reactions with small molecules under ambient conditions (rationalized on the basis that they possess donor/acceptor frontier orbitals separated by modest energies), that led to comparisons of their reactivity with that of open-shell transition-metal species. This rationale, if applied to the synthesis and characterization of new classes of main-group molecules featuring such orbitals, will undoubtedly uncover many new reactions as well as new compound classes. The testing of selected, currently known main-group molecules for reactivity towards small molecules such as H_2 , NH_3 , CO or C_2H_4 may yield several surprises because, until now, it has not been the custom to check the reactivity of main-group species towards small molecules like hydrogen or ethylene. The use of main-group compounds as catalysts, which involve many of these reactions, or as reagents to effect chemical transformations, is also an exciting prospect. Finally, it should not be forgotten that the discovery of the new main-group compounds emerged originally from exploratory inorganic synthesis⁷⁵. Such work continues, and new classes of molecules, such as those with Zn–Zn (ref. 76) and Mg–Mg (ref. 77) bonds or ‘naked’ Si_2 moieties⁷⁸, continue to emerge, which will undoubtedly lead to further advances.

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