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Review

Stretching bonds in main group element compounds—Borderlines between biradicals and closed-shell species

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Contents

Abstract

Biradicals are molecules consisting of two unpaired electrons in two nearly degenerate non-bonding molecular orbitals (NBMOs). They play a central role in bond breaking and formation processes and are usually very short-lived species under standard laboratory conditions. By replacing the carbon-based skeletons of archetypal organic biradicals by main group elements, intriguing mimics of otherwise only transient species are isolable, which can then be characterized by generally applied methods for stable molecules. Nonetheless, the price to pay for gaining stability is the reduction of the biradical character, which makes their designation as biradicaloids more appropriate. Recent advances in the syntheses and characterization of main group element biradicaloids as well as their chemical reactivity and theoretical investigations served as topic of this review article.

Keywords: Biradicals; Biradicaloids; Bond stretch isomers; Reactive intermediates

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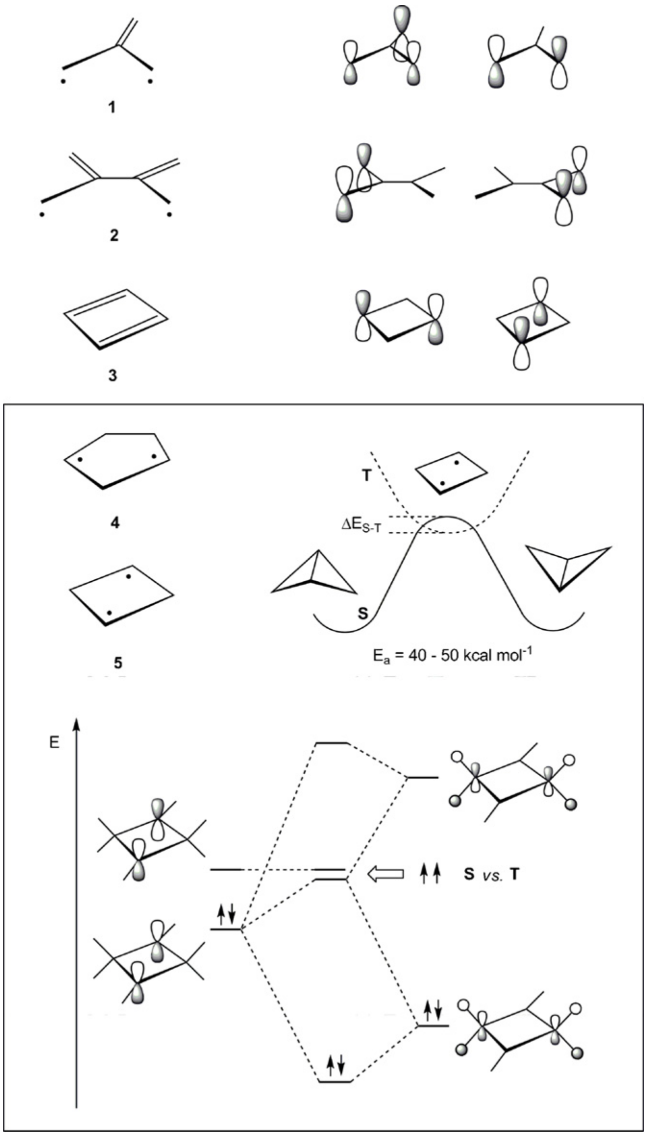
1. Introduction and general comments

1.1. Introduction

Biradicals play a crucial role in bond breaking and formation processes [1]. Many organic biradicals are usually very short-lived species under standard laboratory conditions, which makes their experimental studies difficult. The high reactivity is commonly reflected in recombination of two radical electrons to form a C–C single bond. There are several different types of biradicals. Archetypal delocalized biradicals (non-Kekulé molecules) are trimethylenemethane (TMM, **1**) or tetramethyleneethane (TME, **2**) [2]. Anti-aromatic systems such as cyclobutadiene (**3**) at their geometries of highest symmetry (D_{nh}; $n = 4$ for **3**) are also biradicals consisting of degenerate pair of molecular orbitals (MOs) occupied by two π-electrons. A third class is composed of *localized* biradicals with two well-defined radical substructures that are not conjugated by a π-system such as cyclopentane-1,3-diyls (**4**) or cyclobutanediyls (**5**) (Scheme 1). The orbital interaction scheme for **5** illustrates that a "through-space interaction" between the two radical p-orbitals creates a comparably large HOMO–LUMO gap. A second type of interaction, that is, the filled orbitals of π-symmetry of the bridging methylene units mix (through bond interaction) with the symmetric combination, leads to a (nearly) degenerate orbital set. Depending on the strength of exchange interaction between the two electrons and overall electron correlation within the system, the two electrons can either form a singlet (S) or triplet (T) spin state. In organic biradicals, like cyclobutanediyls (**5**), both spin states are very close in energy ($\Delta E_{\text{S–T}}$ (**5**) = +1.7 kcal mol^{-1}, with the positive sign meaning that the triplet state is preferred) [3]. The triplet states of **5** could be observed by EPR spectroscopy [4] because of the spin forbiddance of ring closure to the corresponding bicyclo[1.1.0]butanes. Singlet cyclobutanediyls were predicted as extremely short-lived transition states for the ring inversion of bicyclo[1.1.0]butanes ($\Delta E = \sim 40–50$ kcal mol^{-1}) [5]. Other organic singlet biradicals could be observed spectroscopically due to increased lifetimes to microseconds upon substituent modification [6].

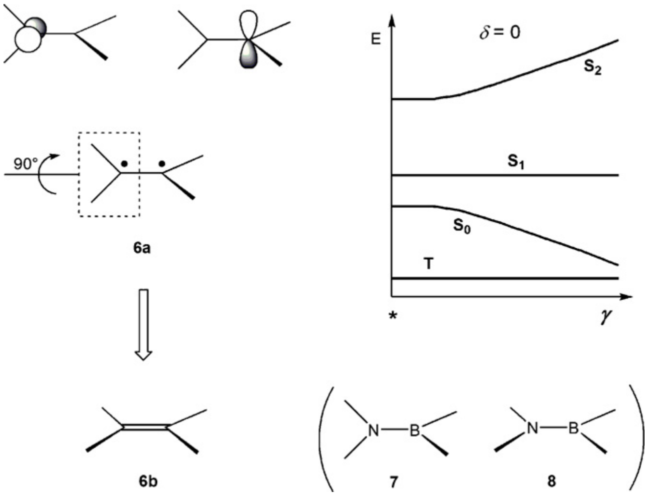


Scheme 1. Delocalized biradicals **1** and **2** and the anti-aromatic system **3** as well as their corresponding orbitals carrying two electrons (top); localized biradicals **4** and **5**; internal reaction profile of the ring-inversion of bicyclo[1.1.0]butanes and schematic potential energy for singlet (S) and triplet (T) surfaces (middle); orbital interaction diagram for **5** obtaining a degenerate HOMO–LUMO pair in dependence of the amount of through-space and through-bond interactions (bottom).

1.2. Spin preference and quantum chemical background

Biradicals share the common feature of two weakly interacting electrons [7], almost independent and of similar energy. As was pointed out by Salem and Rowland [8] both these properties appear to be required of a system in which two radical centers can effectively behave as if they were independent and equally reactive in the presence of an external reagent. Hence, *biradicals are most simply described as molecules consisting of two unpaired electrons in two (nearly) degenerate non-bonding molecular orbitals (NBMOs)*. In terms of spin multiplicity ($2S + 1$) the ground state can either be a low-spin singlet ($S = 0$, anti-parallel spins, anti-ferromagnetic coupling of the spins) or high-spin triplet ($S = 1$, parallel spins, ferromagnetic coupling). If the NBMOs [9] do not span any common atoms and, hence, the two frontier electrons can be confined to separate spatial domains like in square cyclobutadiene (**3**) or TME (**2**), they are classified as disjoint. A typical molecule that features non-disjoint NBMOs is TMM (**1**). Although general rules for the spin preference can be applied to these classes of molecules, a straightforward prediction of the spin state (*S* versus *T*) of biradicals is not possible practically, which seems to be a manifestation of very subtle aspects of the molecular electronic structure [10]. Some general tendencies for the spin preference in biradicals shall be addressed in the next paragraphs. Details can be found in excellent review articles [11].

Although biradicals typically contain more than two electrons and more than two orbitals available to them it is normally possible to describe biradicals by the two-electron two-orbital model [12]. Only two electrons in two approximately non-bonding



Scheme 2. Orthogonally twisted ethylene (**6a**) distorted to planarity (**6b**) yielding a closed-shell molecule (left); schematic drawing of the energies of the singlet (S_x, $x = 0, 1, 2$) and triplet (T) states of a biradicaloid as a function of δ and γ. The asterix indicates the perfect biradical limit ($\delta = \gamma = 0$, see text for details). The energy diagram was adapted from Bonačić-Koutecký, Koutecký, and Michl in Angew. Chem. Int. Ed. 26 (1987) 170. Details can be found there.

(localized or delocalized) orbitals (Φ_A and Φ_B) are considered, disregarding the fixed core. These orbitals can either interact via the one-electron overlap integral S_{AB} and via the two-electron exchange integral K_{AB} as well as the Coulomb part J_{AB}. They are orthogonal (the overlap integral $S_{AB} = 0$) if regions of positive overlap cancel regions of negative overlap, as can be envisaged for instance for the two orbitals in twisted ethylene (**6a**) (Scheme 2). The exchange integral K_{AB} represents the repulsion between the overlap charge density due to the first electron and an identical charge density due to the second electron. The overlap density is large only in those parts in space in which both orbitals have a large amplitude simultaneously. Thus, K_{AB} is a measure of the electron exchange contribution. The physical significance of J_{AB} is the repulsion between the charge density due to an electron in orbital Φ_A and that due to one in orbital Φ_B. From a quantum chemical point of view, a perfect biradical is one in which the real and orthogonal ($S_{AB} = 0$) orbitals Φ_A and Φ_B have equal energies and do not interact. For such a system, three singlet and three triplet wave functions can be composed, to produce a total of six wave functions that satisfy the Pauli principle and represent a complete basis in a two-electron space [13]. The normalized wave functions S_0, S_1, S_2 and T are the energy eigenstates of a perfect biradical (with T = triplet state; S_x = singlet states, $x = 0, 1, 2$) [14]. T is the most stable, S_2 the least stable of all the four states (Scheme 2). For all imperfect biradicals, i.e., those in which the real and orthogonal orbitals Φ_A and Φ_B either interact or have different energies or both, the term biradicaloid (biradical-like) is more appropriate [15]. The gradual conversion of a perfect biradical into a biradicaloid (and eventually into an ordinary closed-shell molecule) can hence be accomplished by introducing certain perturbations, which is accounted for by secondary parameters such as δ_{AB} or γ_{AB}. δ_{AB} is a measure of the energy difference of the orbitals Φ_A and Φ_B while γ_{AB} is a measure of the degree to which they interact. For example, if orthogonally twisted ethylene is gradually returned to planarity: at first, the energies of the localized orbitals are equal ($\delta_{AB} = 0$) and the orbitals cannot interact ($\gamma_{AB} = 0$). When **6a** is distorted towards planarity (**6b**), the energies of the localized orbitals remain equal ($\delta_{AB} = 0$), but they begin to interact ($\gamma_{AB} \neq 0$). This example is a representative of *homosymmetric biradicaloids* [16], for which $\gamma_{AB} \neq 0$ and $\delta_{AB} = 0$, that is, the localized orbitals have equal energies but interact. As γ increases, the S_0–S_1 gap increases relative to that for a perfect biradical and the S_0 state is stabilized relative to the T state (Scheme 2). In fact, the S_0 state may lie below T for even larger values of γ.

It is obvious that for large enough perturbations the two-electron two-orbital system may deviate so much from a perfect biradical that normally it would no longer be considered as biradicaloid. As was pointed out in the literature [11a], the gradual change from the perfect biradical situation to the ordinary closed-shell situation illustrates very nicely the *continuous nature* of the conversion of a biradical into a biradicaloid and eventually into an ordinary molecule by the introduction of a suitable perturbation. However, there is no clear threshold to determine whether a molecule is a biradical, a biradicaloid, or a closed-shell species. The quantities K_{AB} and S_{AB} are very sensitive to geometry and there is no simple way to define limiting values for S_{AB} and K_{AB} beyond which biradical(oid) character [17] is diminished. The main computational estimate for the amount of the biradical(oid) character is the occupation numbers of the natural orbitals (NO). In the ground state of typical closed-shell molecules, all NO occupation numbers are either close to 2 or close to 0. The more closely the NO occupation numbers associated with the two radical sites approaches 1 each, the closer the system is a 'pure' biradical (practically, and thoroughly through this review article, most often LUMO occupation numbers are given) [18]. Again, a definition of a 'pure' biradical based only on NO occupations is practically not possible in an absolute sense, since most (organic) biradicals have LUMO occupation numbers less than one (in some cases they are even around 0.6 e^-). Hence, the NO occupations can just be taken as a kind of scale of the extent of biradical character when compared to other biradicals.

To summarize, the simple picture of two weakly interacting, energetically almost equal electrons is vanished if (a) the overlap integral S_{AB} becomes too large (bond formation: one orbital becomes bonding (HOMO) and is lowered, while the other becomes anti-bonding (LUMO) and is energetically lifted) or if (b) the energy difference between Φ_A and Φ_B is too large (one MO is stabilized and the other is raised: formation of a localized electron-pair in the lower orbital). Hence, for large enough perturbations the two-electron two-orbital system deviates so much from a perfect biradical that its ground-state NO occupation numbers are close to 2 (HOMO) and 0 (LUMO). If the HOMO–LUMO gap is large, the aufbau principle dominates and the system appears like an ordinary closed-shell singlet molecule with two electrons of opposite spin in the HOMO. Examples are twisted aminoborane (**7**, δ_{AB} is large), planar ethylene (**6b**, γ_{AB} is large) and planar aminoborane (**8**, γ_{AB} and δ_{AB} are large, Scheme 2).

Conversely, upon going in the other direction, e.g., upon stretching a bond, scatterings to other singlet states become more accessible and they are able to mix in. In this case, the overall electron correlation becomes important and accordingly the system will increasingly look like a biradical. Usually, the exchange contribution to the energy would unambiguously favour a triplet spin state. If the HOMO–LUMO gap is significant, however, the energy favourability of placing both (anti-parallel) electrons simultaneously into the HOMO will retain the singlet state, but the state is then not completely biradical. Consequently, no ground-state singlet should ever be a perfect biradical, but a singlet wavefunction can show variable biradical character. These Hund's rule and aufbau contributions compete to the same extent at the point when the singlet state and the triplet state are degenerate. According to this, the singlet–triplet energy gap is the best experimental indicator of biradical character. Indeed, singlet biradicals usually show relatively small energy splitting between their lowest energy singlet and triplet state ($\Delta E_{\mathrm{S-T}}$). In addition, they tend to exhibit small splitting between their lowest energy and first excited singlet states, which is associated with a long-wavelength absorption in the UV/vis spectrum. Alongside with the latter, magnetic measurements, cyclovoltammetry (CV), or EPR spectroscopy, which can sensitively detect triplet species, are the most widely used *experimental* indicators of biradical character [19].

1.3. Scope of the review article

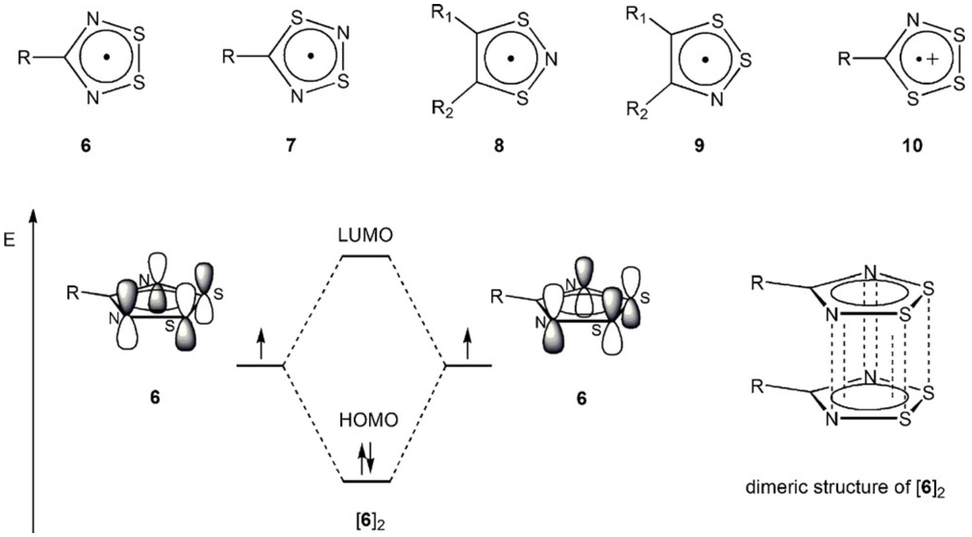
Synthetically accessible molecules with both radical sites in *close spatial proximity* are of fundamental interest because they often resemble the chemists' picture of partly or fully broken bonds. Especially tight geometries like cyclic ring systems featuring two localized radical sites in the same region of space strongly resemble elongated single bonds. By replacing the carbon-based skeletons of organic biradicals such as cyclobutanediyls **5** (in part) by main group elements, intriguing mimics of otherwise only transient species are isolable, which can then be characterized by generally applied methods for stable molecules. Nevertheless, the increasing stability of such species consisting of larger HOMO–LUMO gaps, larger $\Delta E_{\mathrm{S-T}}$, and lower LUMO occupation numbers leads in turn to a less biradical and more closed-shell character, which makes their designation as biradicaloids certainly more appropriate. Recent advances in the syntheses and characterization of main group element biradicaloids (without C) as well as their chemical reactivity and theoretical investigations served as topic of this review article. Main group element monoradicals [20] as well as odd-electron bonds [21] were already summarized elsewhere and will not be discussed here.

2. Sulfur–nitrogen-based systems

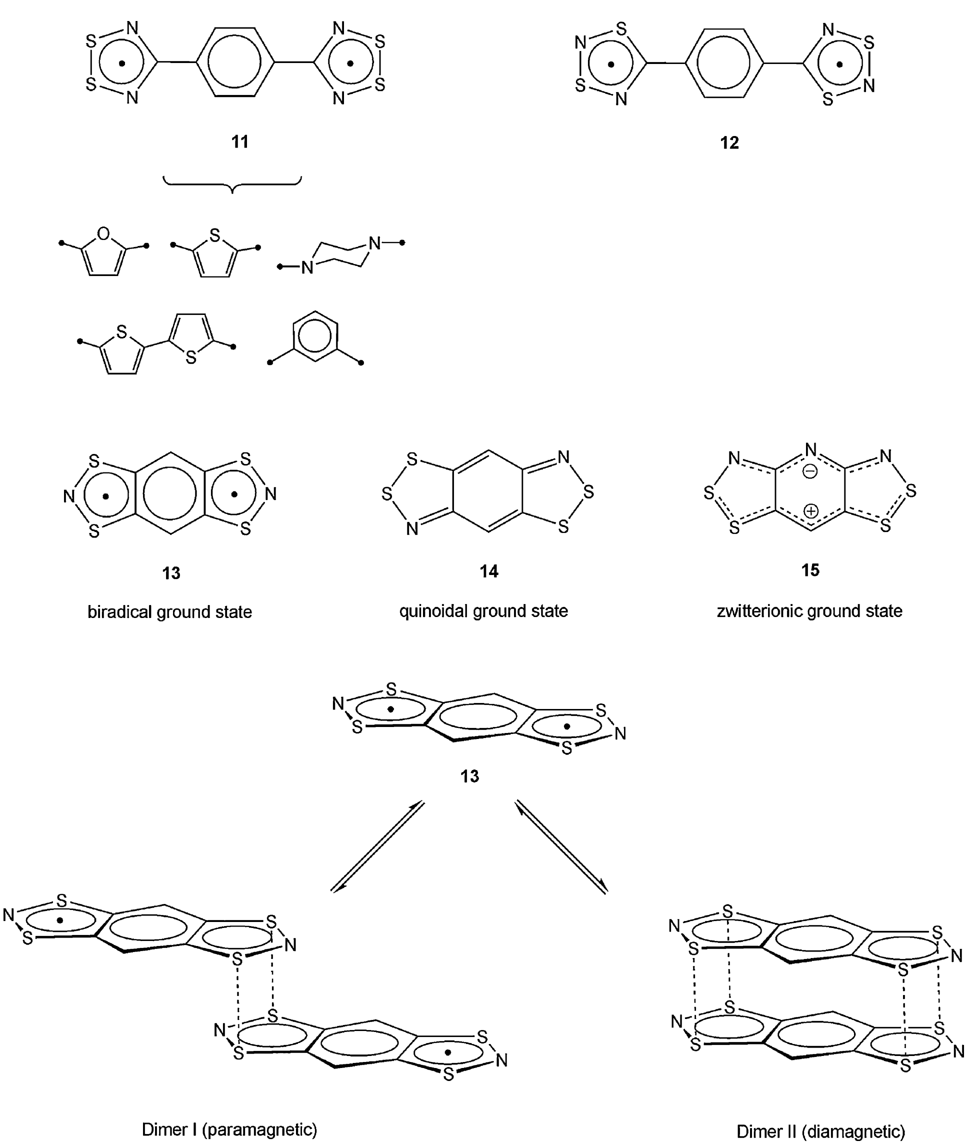
2.1. Thiazyl based biradicals

There has been much effort in exploring and understanding the unusual physical, conducting, and magnetic properties of heterocyclic monoradicals such as thiazyl (and selenazyl) radicals (**6**–**9**) and thiazyl radical cations (**10**, Scheme 3) [22,23]. Most derivatives crystallize in a cofacial π-stacked arrangement as dimers, of which one representative example, i.e. [**6**]$_2$, is shown in Scheme 3. This π^*–π^* association leads to spin pairing in the solid-state, generating a closed-shell diamagnetic ground state. It is important to mention that only selected examples and properties are presented here. For a comprehensive overview the reader is referred to the literature citations.

Fascinating properties were found for linked sulfur–nitrogen radicals (Scheme 4) leading to biradical structures [24]. This class of compounds provide an intriguing opportunity to study the extent of intramolecular electronic exchange effects arising from the presence of two directly tethered radical units. Again, only a selection is presented here in order to demonstrate general tendencies.

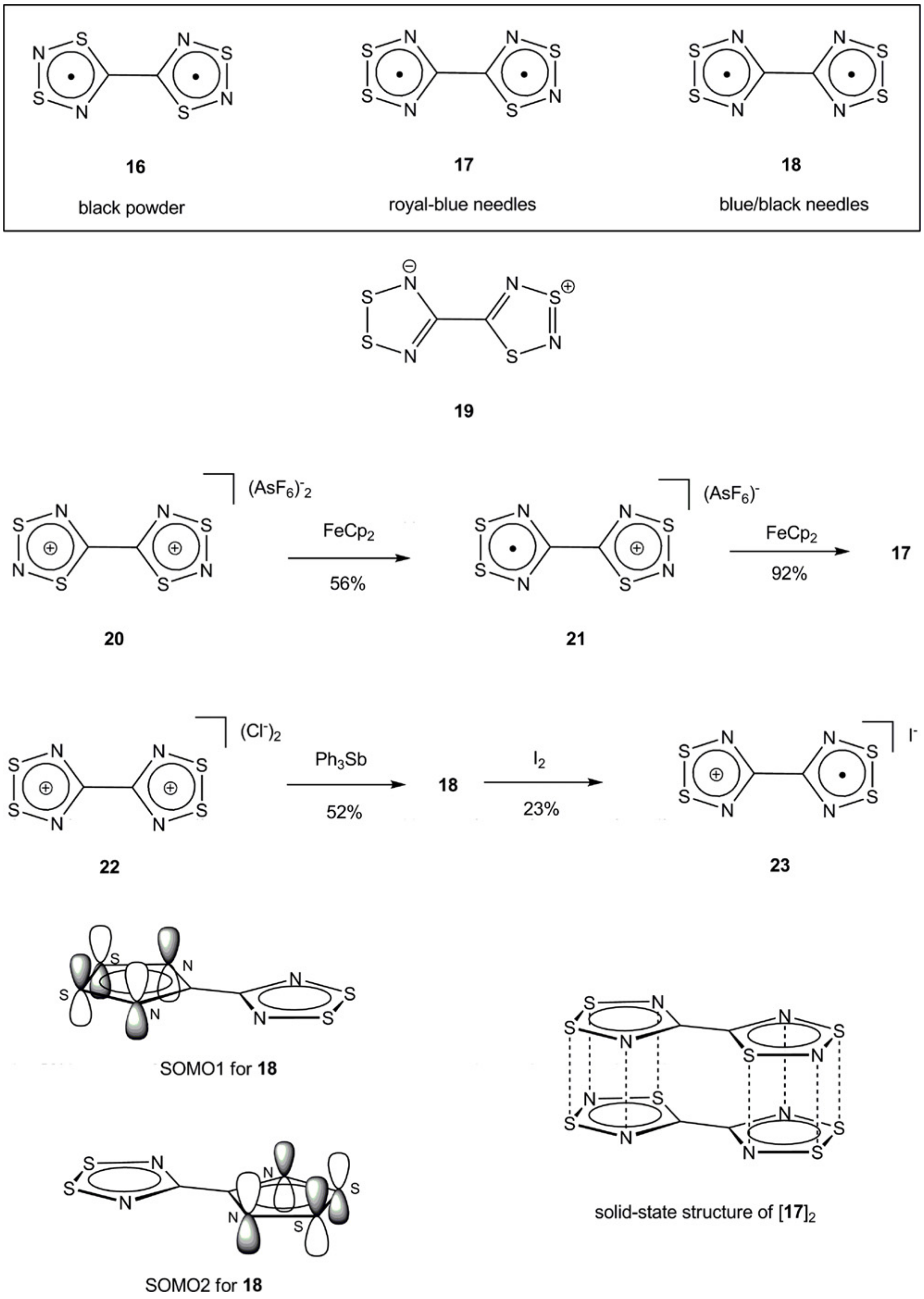


Scheme 3. Thiazyl radicals (**6**–**9**) and radical cations (**10**). For **8** and **9**, annelated ring systems (for R$_1$ and R$_2$) are possible as well (top); dimerization of **6** via cofacial π^*–π^*-interactions leading to a closed-shell dimer [**6**]$_2$ in the solid state; corresponding orbital interaction (bottom, the energy scale (vertical axis) is only qualitative).



Scheme 4. Biradicals **11** and **12** consisting of two linked dithiadiazolyl radical units (top); benzo-1,2:4,5-bis(1,3,2-dithiazolyl) (**13**) and its behaviour in solution; isomeric bis-1,2,3-dithiazole **14** and the corresponding pyridine-bridged species (**15**) showing quinoidal and zwitterionic ground states, respectively (bottom).

Several bis(dithiadiazolyl)biradicals (**11**,**12**) containing various spacing units have been prepared in order to tailor the solid state properties, mainly focused on the design of new materials with interesting properties [25]. Apparently, the radical centres are pushed so far away from each other that no exchange contribution should be likely. Indeed, EPR spectroscopy (triplet pattern, $a_N = 1.1\,\mathrm{mT}$) as well as quantum chemical calculations for **12** predicted the expected disjoint biradical with a triplet ground state [26]. The biradical benzo-1,2:4,5-bis(1,3,2-dithiazolyl) (**13**) has already been pursued by several research groups and the biradical character was identified by EPR spectroscopy [27]. The EPR spectrum is both solvent and sample dependent. For instance, in methylenechloride a typical pattern of simple 1,3,2-dithiazoles, that is, a triplet of triplets ($a_N = 11.3\,\mathrm{mT}$, $a_H = 0.68\,\mathrm{mT}$, $g = 2.0067$) was found, with some broader weak lines in between. However, relative to the concentration of the sample, the overall intensity of the signal was weak, suggesting that the dominant species in solution is of closed-shell type. Since two principle modes of dimerization of **13** are possible in solution, it was supected that the simple triplet of triplets pattern originates from dimer I (Scheme 4) in which the two radical sites are sufficiently removed from one another. Hence, the spectrum should resemble that expected for two separate and non-interacting spin doublets. Dimer II is diamagnetic and should be EPR silent. The broader weak lines were interpreted as an onset of exchange interaction in free, unassociated **13**. Indeed, in toluene a broad pentet was observed which is consistent with that expected for a biradical for which exchange coupling is much greater than the hyperfine coupling to the nitrogen atoms. *Ab initio* calculations revealed that **13** is not formally disjoint, as the corresponding combinations of radical SOMOs mix to different extent with π-type orbitals of the bridging benzene unit. The resulting MOs are essentially not degenerate. However, despite the formal non-degeneracy the two spin states are remarkably close in energy, with the singlet lying slightly above the triplet ($0.5\,\mathrm{kcal\,mol^{-1}}$).



Scheme 5. Syntheses of bis(dithiadiazolyl)biradicals and related radical cations; disjoint biradical **18** (SOMOs); unprecedented solid-state structure of (**17**)$_2$ (secondary dimer–dimer interactions in the solid-state between various dimeric units are not shown).

Cyclovoltammetric investigations for **13** revealed two reversible oxidation waves ($E^0_{1/2,\mathrm{SCE}} = 0.16$ V: **13** → [**13**]$^+$; $E^0_{1/2,\mathrm{SCE}} = 0.74$ V: [**13**]$^+$ → [**13**]$^{2+}$). While the benzo-bis(1,3,2-dithiazole) **13** is a biradical, the isomeric bis-1,2,3-dithiazole **14** exhibits a quinoidal rather than a biradical ground state [28]. Interestingly, Oakley and co-workers found the pyridine-bridged compound **15** to be a zwitterion [29].

In contrast, the "back-to-back" biradicals **16**–**18** shown in Scheme 5 do not adopt classical Lewis structures in which the Lewis octet rule is obeyed (see, e.g., **19**). Instead, they have a thermodynamic preference for structures containing two unpaired electrons [30]. The highly colored biradicals are accessible by reduction of the corresponding dications (**20**) with ferrocene ($\mathrm{FeCp_2}$) or by well-established procedures such as treatment of the precursor with triphenylantimony in refluxing acetonitrile. According to Cordes, Haddon, and Oakley [31], biradical **18** is a rare example of a disjoint biradical, in which the molecular orbitals for the two unpaired electrons can be localized to separate groups of atoms (SOMO1 and SOMO2 in Scheme 5). For disjoint

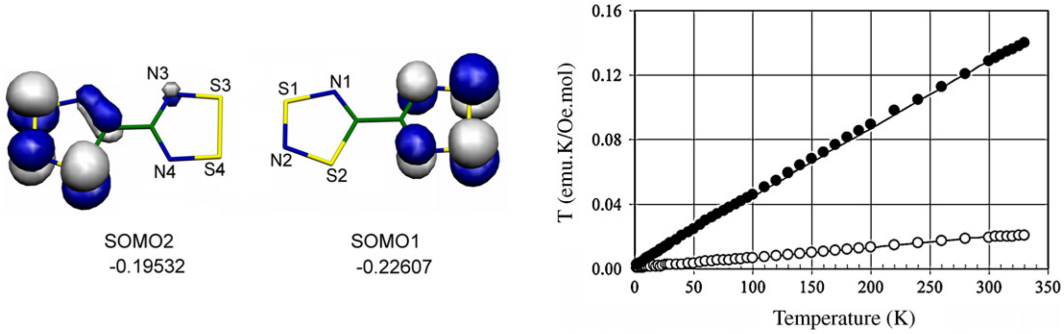


Fig. 1. Calculated SOMOs of **17**; $\Delta E = E_{\mathrm{SOMO2}} - E_{\mathrm{SOMO1}} = 81\,\mathrm{kJ\,mol^{-1}}$ (left); temperature dependence of χ^{T} for a sample before (○) and after (●) grinding. The solid lines correspond to fits to a Curie-paramagnet with a temperature-independent paramagnetic (TIP) term ($\chi = C/T + \mathrm{TIP}$). Reprinted with permission from Cameron et al. [32a]. Copyright (2005) American Chemical Society.

biradicals exchange interactions between the two centres are small, and the singlet–triplet gap ($\Delta E_{\mathrm{S\text{-}T}} = -0.50\,\mathrm{kcal\,mol^{-1}}$ (planar); $-0.55\,\mathrm{kcal\,mol^{-1}}$ (twisted, 90°)) is very small—the two states are essentially degenerate. Cyclovoltammetric investigations of the dicationic precursor **22** revealed a reversible dication/biradical reduction wave at $E^{0}_{1/2,\mathrm{SCE}} = 0.68\,\mathrm{V}$ and an irreversible biradical/dianion reduction wave near $E^{0}_{1/2,\mathrm{SCE}} = -0.80\,\mathrm{V}$. The first reduction process showed a peak-to-peak separation of 98 mV, which may indicate two slightly interacting one-electron reductions ("communication") rather than a single two-electron step. The five-line pattern of the EPR spectrum of **18** at 273 K ($g = 2.011$, $a_{\mathrm{N}} = 0.5\,\mathrm{mT}$) suggested virtually no exchange interaction, whereas, at 303 K some features associated with the onset of exchange coupling were detected. As was reported recently by Passmore and co-workers [32], the previously unknown, mixed ($^{\bullet}$NSSNC–CNSNS$^{\bullet}$) biradical **17** should be considered as a pseudo-disjoint biradical as there is no nodal plane along the long axis of the molecule (see SOMOs in Fig. 1).

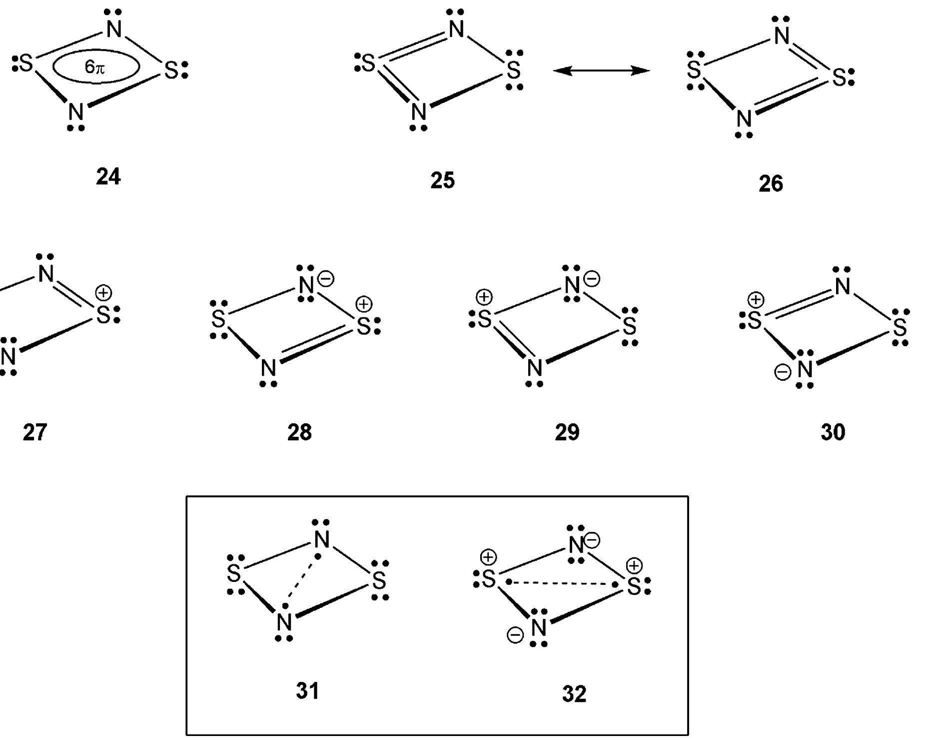
Consisting of a partial contribution of SOMO2 (Fig. 1) to both dithiadiazolyl rings an enhanced exchange contribution may be anticipated. However, the EPR of **17** in SO_2 yielded only the anticipated triplet ($g = 2.00413$, $a_{\mathrm{N}} = 1.03\,\mathrm{mT}$). **17** shows interesting properties in the solid-state. Firstly, molecules of **17** form π^*–π^* dimers of an almost unprecedented mode, with two molecules displaced about an inversion centre such that π^*–π^* interactions between different isomeric rings are observed (see Scheme 5). Secondly, magnetic measurements of **17** indicated essential diamagnetism (due to coupling of the radical sites by π^*–π^* interactions in the solid-state) with the room-temperature susceptibility corresponding to just 5% of unpaired spins (Curie centres $C = 0.00035$, temperature-independent paramagnetic term $\mathrm{TIP} = 6.5 \times 10^{-5}\,\mathrm{emu\,Oe^{-1}\,mol^{-1}}$). The paramagnetism of **17** (as for **16**) is essentially increased upon grinding ($C = 0.003$, $\mathrm{TIP} = 4.2 \times 10^{-4}\,\mathrm{emu\,Oe^{-1}\,mol^{-1}}$). As reported by Passmore and co-workers, the grinding likely provides the energy needed to overcome the activation barrier of the transition from the diamagnetic to the thermodynamically more stable paramagnetic phase. In summary, these exciting compounds belong to a rare class of non-sterically hindered biradicals from which interesting applications such as low-dimensional molecular conductors may arise.

2.2. S_2N_2 and related compounds

The electronic structures of seemingly simple molecules such as E_2N_2 or E_4^{2+} (with E = S, Se, Te) turned out to be rather complex and have therefore been the focus of many theoretical investigations [33].

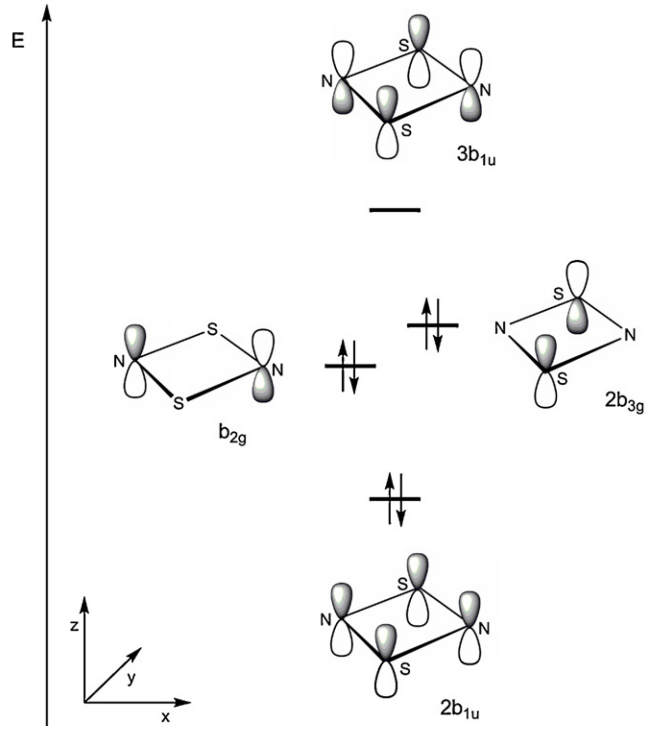
Out of these, the electronic structure of S_2N_2 has most often been discussed in the literature ranging from a 6π-electron aromatic system (**24**) as well as symmetry-broken (**25** and **26**) and zwitterionic Lewis structures (**27**–**30**) to the spin-paired biradical structure **31** with a long N···N bond across the ring and the sulfur centered singlet biradical structure **32** (Scheme 6) [34]. The molecular orbital (MO) analysis of the six-electron π-system given in the literature is depicted in Scheme 7. In addition to four σ-bonding MOs (not shown) the four p_z orbitals of S and N give one π-bonding MO ($2b_{1u}$), two non-bonding MOs (b_{2g} and $2b_{3g}$) and one anti-bonding MO ($3b_{1u}$) consisting of 0, 1, or 2 nodal planes perpendicular to the ring plane, respectively. The two non-bonding orbitals of similar energy are HOMO and HOMO-1, whereas, the anti-bonding MO $3b_{1u}$ is the LUMO. The occupied MOs b_{2g} and $2b_{3g}$ are non-bonding and the bonding MO $2b_{1u}$ is interpreted as a 4c–2e π-bond. The delocalization of these two π-electrons leads to the aromatic [35] characteristics (NICS = −26.2 ppm; aromatic stabilization energy ASE = $6.5\,\mathrm{kcal\,mol^{-1}}$ (cf. −25.4 ppm and $33\,\mathrm{kcal\,mol^{-1}}$ for benzene); NICS = nucleus-independent chemical shift; a direct measure for aromaticity) [36,37]. Despite the presence of six π-electrons in the electronic structure, only two of these electrons participate in (π) bonding. The total bond order for each individual S–N bond is therefore 1.25 (WBI = 1.212, B3LYP/6-311 + G(d)), which is slightly less than concluded from the experimental bond length of 165.4 pm.

Despite the fact that no general agreement of the electronic structures of tetraatomic square-planar molecules like S_2N_2 has yet been reached, the singlet biradicaloid forms of S_2N_2 have been addressed by a few authors. Calculations of Skrezenek and Harcourt [38] suggest that the singlet biradical character of S_2N_2 is associated more with the nitrogen atoms (**31**) than with the sulfur atoms (**32**) and that the four zwitterionic Lewis structures **27**–**30** make smaller contributions to the ground-state resonance scheme. This is in line with results presented by Suontamo and



Scheme 6. Different electronic structures and bonding pictures proposed in the literature for S_2N_2.

co-workers [39] giving the largest weight to the singlet biradical Lewis-type VB structure in which the unpaired electrons reside on the nitrogen atoms (**31**). Furthermore, they found an increase of the biradical character in E_2N_2 (and isoelectronic E_4^{2+}) upon descending the group. From multiconfigurational CASSCF calculations the biradical character of S_2N_2 was calculated to 6%, whereas, Te_2N_2 has nearly 10% biradical character. Recent calculations of Head-Gordon and co-workers [40] on the aromaticity of four-membered-ring 6π-electron systems like S_2N_2 revealed large HOMO–LUMO (119.9 kcal mol^{-1}) and singlet–triplet ($\Delta E_{S-T} = -83.0$ kcal mol^{-1}) gaps. Although relatively large LUMO occupation numbers of 0.12 e$^-$ (VOD (22,22)) and 0.20 e$^-$ (CASSCF(6,4)) were calculated for S_2N_2, the authors emphasized that these values indicate only quite strong non-bonding to anti-bonding correlation but they are not directly associated with 12% (or 20%) biradical character [41]. Furthermore, they concluded that S_2N_2 should be regarded as a 2π-electron aromatic system with approximately 93% aromatic character. However, as can be seen by the diverging opinions in the literature, the relative importance of the different VB structures seem to be highly dependent on the level of theory. Whatever the final conclusion about the electronic structure will be, all theoretical analyses demonstrate that the simple view of cyclic delocalized electrons as described by the resonance structure **24** is certainly an oversimplification of the bonding in E_2N_2 and E_4^{2+}.

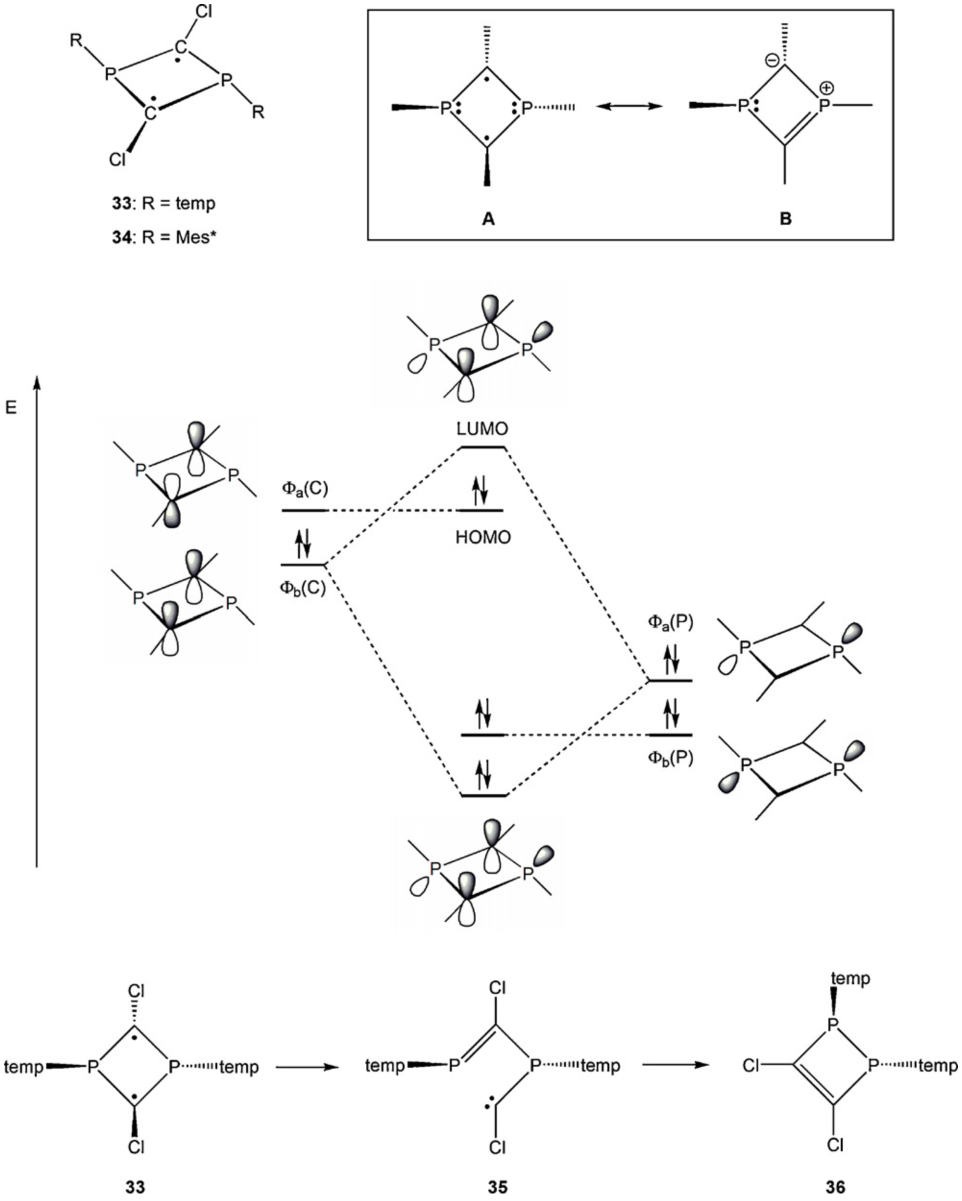


Scheme 7. Molecular orbital (MO) diagram of the π-system in S_2N_2 built up from four p_z orbitals of sulfur and nitrogen: one bonding π MO $2b_{1u}$, two non-bonding MOs b_{2g} and $2b_{3g}$ and one anti-bonding MO $3b_{1u}$. The energy scale (vertical axis) is only qualitative.

3. Phosphorus–carbon-based compounds

3.1. Syntheses of Niecke-type biradicals

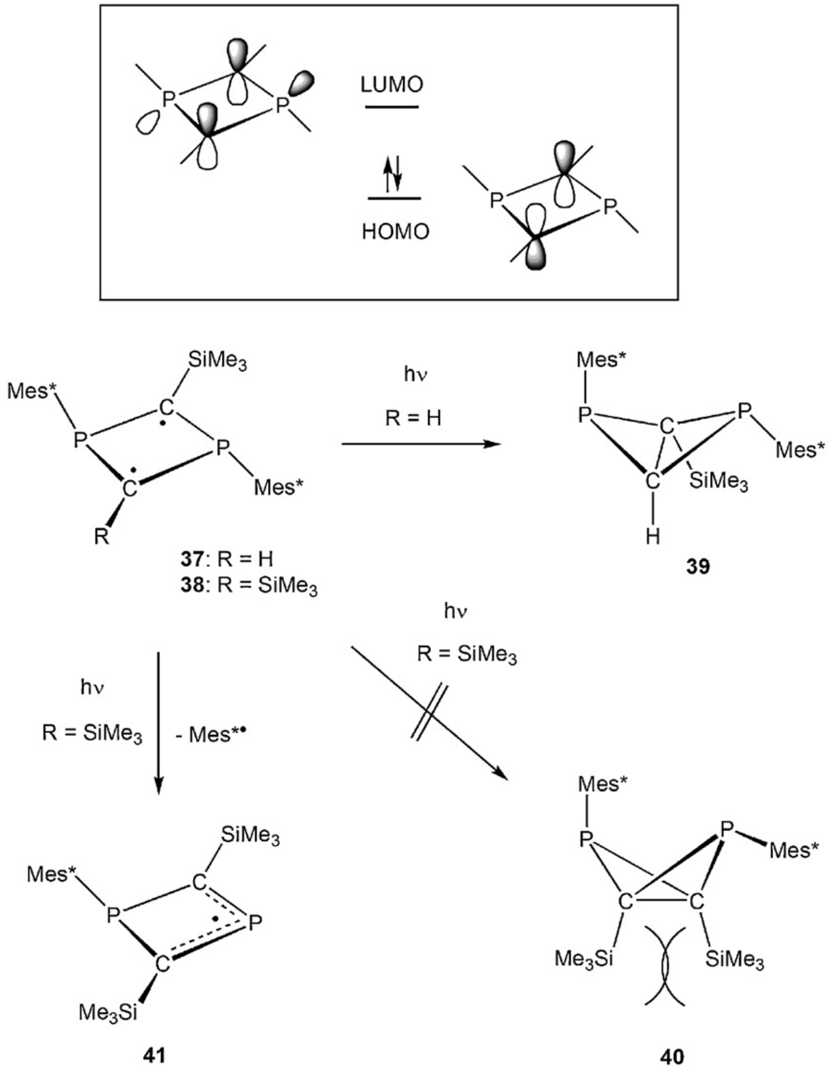
Isolobal replacement of the nitrogen constituents in S_2N_2 by CR moieties and the sulfur atoms by PR groups leads to formally isoelectronic 1,3-diphosphacyclobutane-2,4-diyls, $(RP)_2(CR)_2$. Such phosphorus–carbon based biradicaloid species are



Scheme 8. 1,3-Diphosphacyclobutan-2,4-diyls (**33**, **34**; with temp = 2,2,6,6-tetramethylpiperidyl; Mes* = 2,4,6-*t*-$Bu_3C_6H_2$) and resonance structures **A** and **B** (top); mixing of one of the carbon orbitals (Φ_b(C)) with one of the corresponding combinations of lone pair orbitals at phosphorus (Φ_a(P)) (middle; the energy scale (vertical axis) is only qualitative); isomerization of **33** to the dihydrodiphosphete **36** via a phosphanylcarbene **35** (bottom).

accessible from the reaction of *C*-dichlorophosphaalkenes with *n*-BuLi at −100 °C (Scheme 8) [42]. However, a closer inspection of the electronic structure of 1,3-diphosphacyclobutane-2,4-diyls reveals that they are electronically different from S_2N_2. The sulfur atoms in S_2N_2 can form outward pointing s-orbitals, whereas, the p-electrons are utilized for ring bonding. Instead, the P atoms in the phosphorus analogue bear ligands, which enforce a pyramidalization. The ring skeleton of these unusual P_2C_2 heterocycles is planar featuring (weakly) pyramidalized coordination spheres both at the carbon and the phosphorus centres. The reasonably high inversion barrier at phosphorus impede the formation of a planar 6π-conjugated heterocycle. As a consequence, the LUMO occupation number of 0.4 e^- as well as the small singlet–triplet energy gap ($-\Delta E_{S-T}$) of 6.2 kcal mol^{-1} (CAS(14,12)/6-31g(d,p)) [43] suggested considerable biradicaloid character. On the other hand, the environment at the P atoms is less pyramidal than in common phosphanes, which indicates some degree of π-donation from the phosphorus lone pairs to the carbon radical centers. The stabilization of the singlet state can be explained by a conjugative interaction of the unpaired electrons at the C atoms with the non-bonding electron pairs at the P atoms. The electronic ground state may be approximated by the resonance structures **A** and **B** shown in Scheme 8 and diphosphacyclobutane-2,4-diyls may be described as weak π-conjugated biradicaloids.

The P-amino derivative **33** is unstable at room temperature and isomerizes rapidly and quantitatively in solution, and slowly even in the solid state, to the 1,2-dihydrodiphosphete **36**. Quantum chemical calculations (MCSCF-(10,10)/6-31G(d)) revealed that the isomerization of **33**–**36** is a two-step process



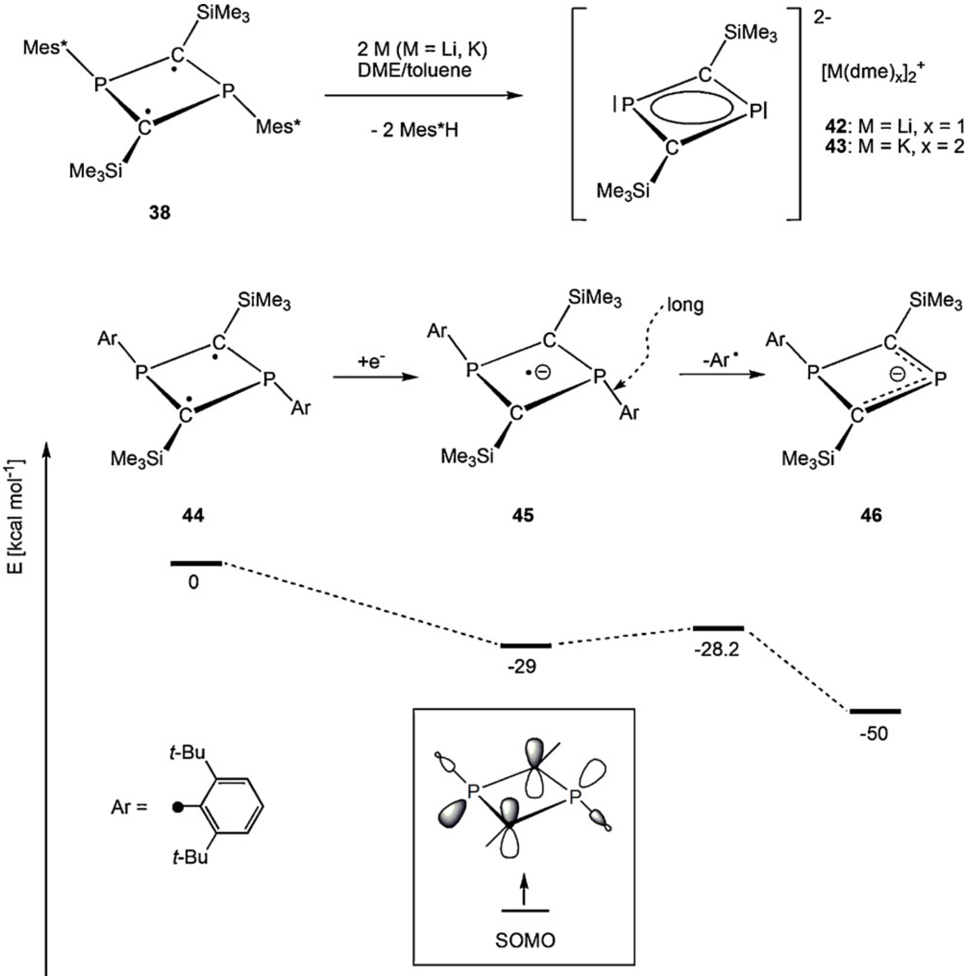
Scheme 9. Different photochemical behaviour of 1,3-diphosphacyclobutane-2,4-diyls: (a) photolytical ring closure to the thermodynamically more stable valence isomer 2,4-diphosphabicyclo[1.1.0]butane **39** (with R = H); (b) homolytical P–C_{aryl} bond cleavage and formation of 1,3-diphosphetane-2-yl **41** (R = $SiMe_3$).

consisting of a singlet phosphanylcarbene (**35**) as intermediate [44].

3.2. Reactivity of Niecke-type biradicals

Since the pioneering work of Niecke concerning these biradicals numerous exciting reactions have been performed, mainly driven by the extraordinary stability and simple accessibility of some derivatives. By varying the substituents, the biradicaloids become stable against isomerization under ambient conditions, which has facilitated the examination of their chemical behaviour. For instance, the chloro substituents in **34** can be exchanged by $SiMe_3$ and hydrogen to give **37** [45]. This red crystalline compound comprising trigonal planar C environments and a planar P_2C_2 heterocycle within its molecular core is thermally stable and not affected by short heating to 150 °C. However, photolysis of red **37** leads almost quantitatively to yellow **39** (Scheme 9). The X-ray crystal structure of **39** revealed a transannular carbon–carbon bond of 151.6 pm and a interflap angle of the P_2C_2 ring of 117°. This is in agreement with Niecke's *ab initio* MCSCF calculations [42] on the parent system $(PH)_2(CH)_2$—the symmetries of the frontier orbitals (Scheme 9) do not allow a thermal but a photolytical ring closure of the open P_2C_2 heterocycle to the thermodynamically more stable valence isomer 2,4-diphosphabicyclo[1.1.0]butane **39**.

The formation of the bicyclic compound can be suppressed by employing sterically more demanding $SiMe_3$ substituents on both carbon atoms (**38**). Note that a ring closing procedure for **38** is a disrotatory process, which would result in (large) steric interactions of two $SiMe_3$ groups in close spatial proximity in the bicycle **40**! Indeed, under photochemical conditions one P–C_{aryl} bond within **38** (R = $SiMe_3$) is homolytically cleaved under formation of supermesityl radicals ($Mes^{*\bullet}$) and the phosphaallyl radical **41** (Scheme 9), which dimerizes under P–P bond formation (not shown) [46]. Since the P–C_{aryl} bond is easily cleaved upon irradiation an aniomesolytic fragmentation tendency under reducing conditions was anticipated, that is, $Mes^{*\bullet}$ succession



Scheme 10. Synthesis of diphosphacyclobutadiendiides **42** (M = Li) and **43** (M = K) (top); Calculated energy profile of the reduction of 1,3-diphosphacyclobutane-2,4-diyls and homolytical P–C_{aryl} bond cleavage (bottom). DME = 1,2-dimethoxyethane.

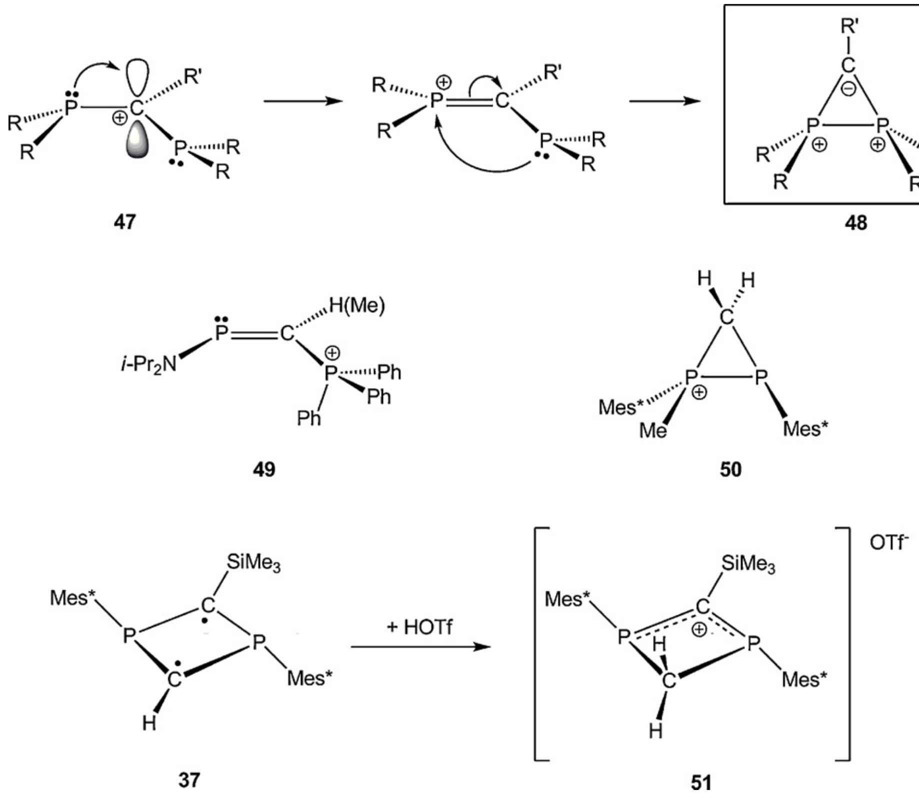
upon treatment of **38** with elemental alkali metal (Eq. (1)).

$$[(PMes^*)_2(CR)_2] + e^- \rightarrow [(PMes^*)_2(CR)_2]^{-\bullet} \rightarrow [P(PMes^*)(CR)_2]^- + Mes^{*\bullet} \quad (1)$$

As expected, the reaction of **38** with two equivalents of lithium or potassium in dimethoxyethane (DME)/toluene afforded red reaction mixtures from which the dianions **42** (M = Li) and **43** (M = K) were isolated in high (>90%) yield (Scheme 10) [47].

The X-ray crystal structure of the lithium salt (**42**) revealed a monomeric ion pair featuring a planar, C_1-symmetric P_2C_2 heterocycle with both lithium cations located above and below the central unit, each coordinated by an additional DME solvent molecule. The Si–C(P_2)-bond lengths (181.9 pm) are somewhat shorter than observed in silyl-substituted cyclobutadiene dianions [48]. This can be attributed to p(C) → σ^*(Si) back bonding (negative hyperconjugation), which was supported by ^{29}Si NMR investigations (δ ^{29}Si = −17.3 ppm). Since the tendency of phosphorus to conjugate with carbon in π-systems is well known, the aromaticity of the 1,3-diphosphacyclobutadiendiides, $[P_2(CR)_2]^{2-}$, should be comparable to the analogous carbon systems, $[(CR)_4]^{2-}$, which was recently published by Sekiguchi et al. [48]. Quantum chemical calculations for the lithium compound **42** revealed a NICS value of −7.0 ppm (B3LYP/6-311 + G**//B3LYP/6-31 + G*), which is slightly smaller than −9.2 ppm calculated for $[\{Li(DME)\}_2\{CSiMe_3\}_4]$. Schleyer and co-workers found even more negative values of up to −23.7 ppm for the dilithiated species $Li_2C_4R_4$ (R = H, Me, *t*-Bu) [49]. These differences may be attributed to the silyl substituents, which lower the π-electron density within the cyclic core. Nevertheless, the dianions ($4n + 2\pi$-electrons) revealed to be aromatic (negative NICS values) [37].

In order to shed some light on the mechanism of this reaction, further calculations were performed which are summarized in Scheme 10 (bottom). Upon reduction of **44** a radical anion (**45**) is generated which is 29 kcal mol^{-1} more stable. Interestingly, although the main structural features of both compounds are almost the same (except that all bonds in **45** are somewhat longer), **45** shows an especially long P–Ar bond of 194 pm (with Ar = 2,6-*t*-$Bu_2C_6H_3$). This can be explained by a single occupation of the frontier orbital (SOMO) of **45**. Although the SOMO is located to a large extent at the P_2C_2 ring atoms, it

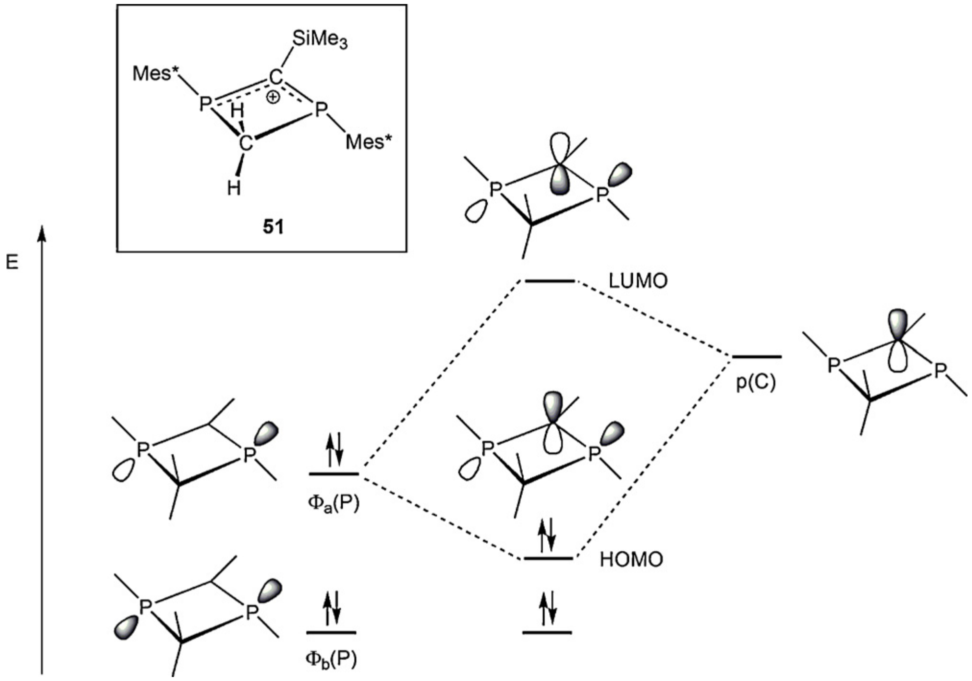


Scheme 11. Open form of the diphosphino-substituted carbocation **47** and the cascade stabilization to its cyclic carbanionic valence isomer **48** (top); literature known isomers of **47**: phosphonium-substituted phosphaalkene **49** (only one substituent pattern shown; see Ref. [50] for details) and a diphosphiranium salt **50** (middle); synthesis of a cyclic bis(phosphanyl)carbenium ion **51** via protonation of a 1,3-diphosphacyclobutane-2,4-diyl 37 (bottom). $OTf^- = SO_3CF_3{}^- =$ triflate.

comprises a significant anti-bonding (σ^*_{PC}) character of the terminal P–C_{aryl} bond (Scheme 10). Thus, the P–Ar σ-bond is considerably weakend. The anticipated aniomesolytic fragmentation ($[(PAr)_2(CR)_2]^{-\bullet} \rightarrow [P(PAr)(CR)_2]^- + Ar^\bullet$) occurs in a second step furnishing the cyclic phosphaallyl anion **46**, which is 21.1 kcal mol^{-1} more stable than the intermediate **45**. The postulated mechanism for the formation of the dianion **42** involving a cyclic phosphaallyl anion was experimentally verified by ^{31}P NMR spectroscopy upon reduction of **37** (with one H and one $SiMe_3$ substituent) with one equiv. of lithium metal.

Niecke's 1,3-diphosphacyclobutane-2,4-diyls revealed to be valuable precursor compounds for the synthesis of otherwise unknown structural motifs such as the open form of bis(phosphanyl)carbocations (**47**). The latter are formally equivalent to allyl anions featuring a 3c–4π-electron system. Although some isomers (**49** and **50** in Scheme 11) [50,51] of 1,3-bis(phosphanyl)carbenium ions have been synthesized some years ago, carbocations of the general formula **47** were unknown until recently. This is mainly due the intrinsic characteristics of phosphorus, which avoids the formation of multiple bonds and trigonal planar coordination spheres [52]. Hence, only the cyclic carbanionic valence isomer **48** of the open carbocation structure is formed, as was shown by Bertrand and co-workers recently [53]. Compound **48** can be considered as resulting from a cascade stabilization of the electron-deficient carbocation center as depicted in Scheme 11. In the corresponding amidinium ions, $[CR'(NR_2)_2]^+$, the electronegativity causes the N atom to remain negatively charged although the amino group stabilizes the central carbocation by electron donation from the N lone pairs. However, the bond polarities are reversed by substituting NR_2 (δ−) with a phosphanyl group PR_2 (δ+). As in the case of monophosphino carbenium ions, the first phosphorus atom donates electrons to the carbocationic center and becomes positively charged and highly electrophilic. The second P atom then acts as a Lewis base towards the first.

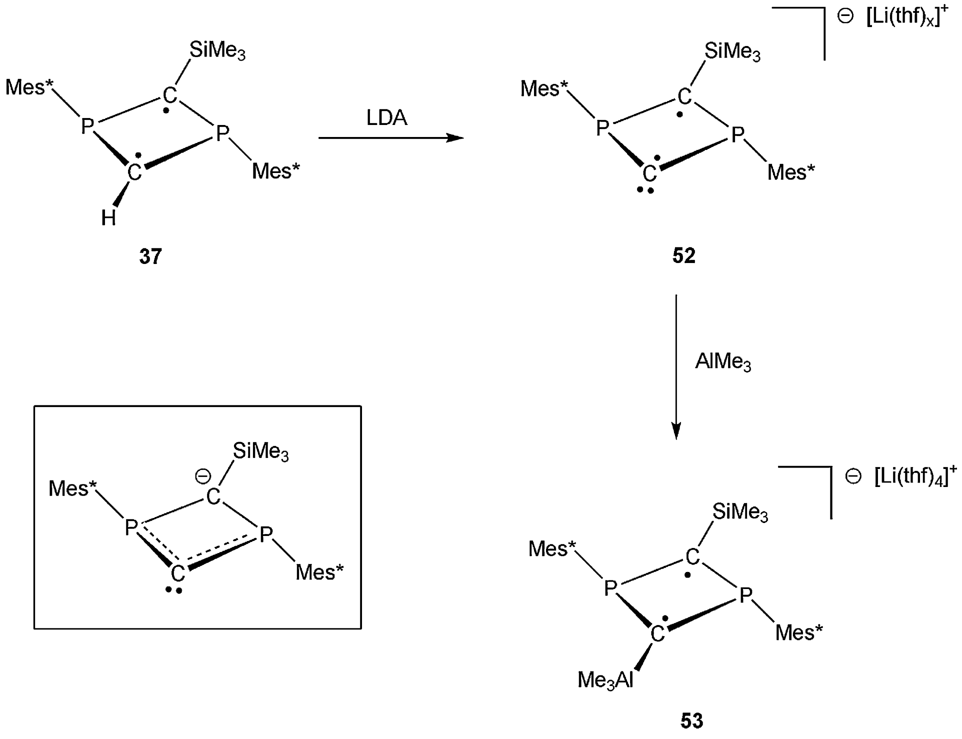
The P–P-bond formation, however, can be suppressed simply by integrating the P–C–P-subunit into a small heterocyclic ring structure like in **37**, as was impressively shown by Niecke and co-workers. The bis(phosphanyl)carbenium salt **51** (with OTf-counteranion) is straigthforwardly accessible by protonation of the 1,3-diphosphacyclobutane-2,4-diyl **37** with one equiv. of triflic acid (HOTf) in toluene [54]. The X-ray structure analysis as well as NMR chemical investigations revealed only a slight alteration of the central P_2C_2 ring geometry suggesting a delocalization of the positive charge in an allyl-type system (see Scheme 11). As can be seen from the schematic representation of the frontier orbitals in Scheme 12, the LUMO is located at the silyl substituted carbon atom featuring a considerable contribution of the lone pairs at the pyramidal P atoms. This is explained by an interaction of the anti-bonding combination (Φ_a(P)) of suitable symmetry with the empty carbon p orbital. Quantum chemical calculations predicted an overall stabilization of ∼132 kcal mol^{-1} (B3LYP/6-31 + G*) with respect to the undelocalized carbocation.



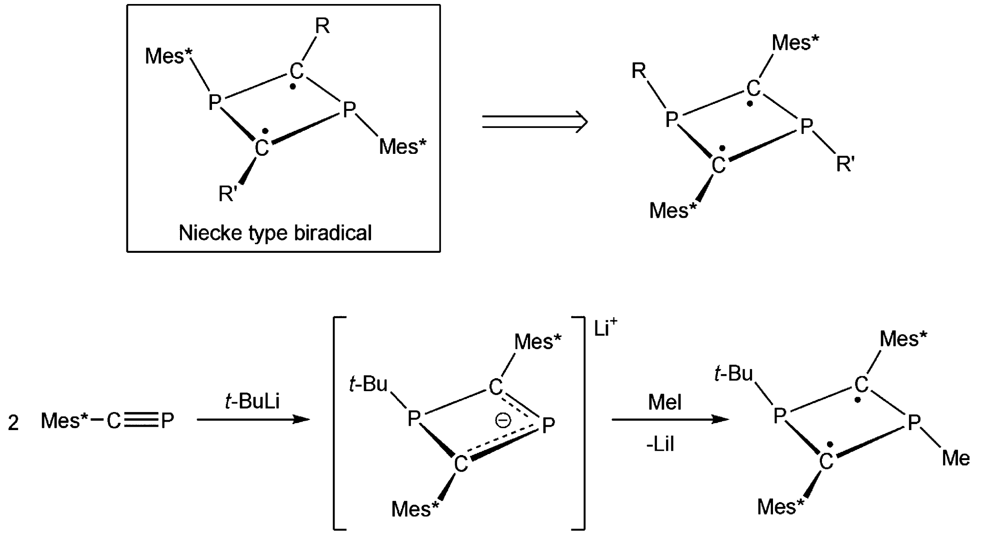
Scheme 12. Stabilizing interactions between the lone-pairs at the P atoms and the empty p-orbital of the carbocation. The energy scale (vertical axis) is only qualitative.

In addition to protolysis, the 1,3-diphosphacyclobutane-2,4-diyls are readily deprotonated. Unprecedented carbenes are accessible by deprotonation of **37** with one equiv. lithium diisopropylamide (LDA) yielding intensively red colored solutions of anionic **52**, which can be reacted with the Lewis acid $AlMe_3$ to give the adduct **53** (Scheme 13) [55].

The X-ray crystal structure analysis of the trimethyl aluminium adduct **53** revealed the central P_2C_2 ring to be planar with the non-carbene C-atom slightly pyramidalized (sum of the bond angles = 357.4°). *Ab initio* calculations of the model compound *cyclo*-$[P(CH_3)–C(SiH_3)P(CH_3)C]^-$ predicted both carbon atoms to be negatively charged. The 1,3-



Scheme 13. Synthesis of 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide **52** via deprotonation of a 1,3-diphosphacyclobutane-2,4-diyl **37** and its trimethyl aluminium adduct **53**.



54 **55**

Scheme 14. Synthesis of sterically protected (Mes*) 1,3-diphosphacyclobutane-2,4-diyls (**55**) starting from a phosphaalkyne according to Yoshifuji and co-workers.

diphosphacyclobutane-2,4-diyl-2-ylidenide **52** can be described as cyclic, anionic bis(phosphanyl)carbene, which is stabilized by p-electron density of the carbanionc C-atom (see inset of Scheme 13). The singlet–triplet energy gap of the carbene was calculated to 7.4 kcal mol^{-1}.

Recently, Yoshifuji and co-workers reported on a novel synthetic strategy for a high yield synthesis of various 1,3-diphosphacyclobutane-2,4-diyls starting from a phosphaalkyne (Scheme 14) [56]. Interestingly, these derivatives, comprising the large aryl ligands on the C instead of the P atoms like in Niecke-type biradicals, are even stable in air. The UV/vis absorption of 612 nm (cf. 478 nm for **34**) [42] clearly indicates that the energy splitting between the lowest energy and first excited singlet states is small. Although no HOMO/LUMO occupation numbers and singlet–triplet splitting (ΔE_{S-T}) were reported for these compounds an increased biradical character may be anticipated. However, the radical centers in **55** are effectively protected by the sterically demanding Mes* residues. This elegant method enables various kinds of nucleophiles and electrophiles to be employed in the reaction described in Scheme 14. Commonly, *t*-butyl lithium is used to prepare the intermediate **54** but other nucleophiles such as lithium diisopropylamide are also appropriate. The second P atom can be substituted either by using simple alkyl halides as well as benzyl- or benzoyl chloride. First investigations concerning the reactivity of these diyls revealed interesting ring-opening, valence isomerization, and ring-expansion reactions reflecting their high synthetic potential [57].

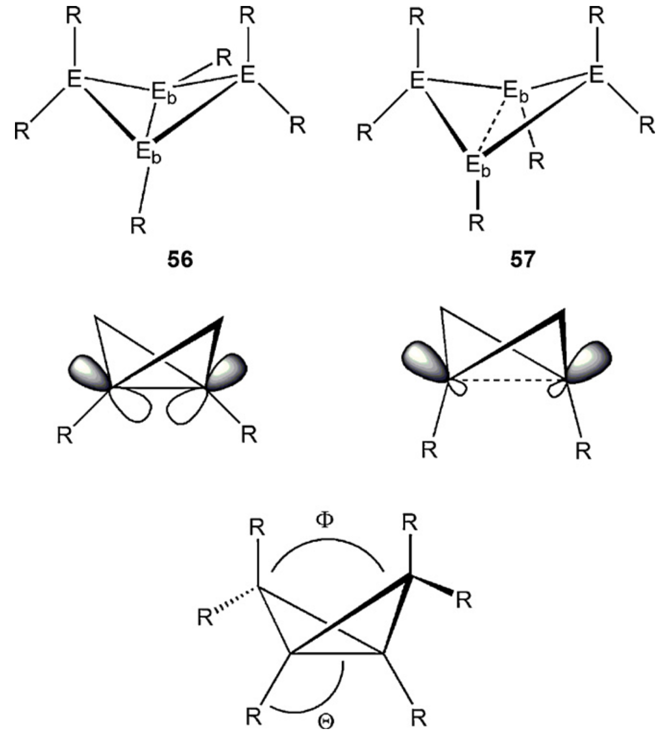
4. Group 14 element systems

4.1. Bicyclo[1.1.0]butanes E_4R_6 and related compounds

Strained, bicyclic structures of Group 14 element compounds have been of increased interest [58], because they were identified as suitable candidates for the synthesis of stable biradicaloids. For the heavier congeners of bicyclo[1.1.0]butanes, several quantum chemical calculations [59] predicted the phenomenom of bond stretch isomerism, that is two distinct minima on the potential energy surface which mainly differ by the length of one bond, as a result of the high ring strain and intrinsically low σ-bond energies. The topic of bond stretch isomerism was recently summarized by Rohmer and Bénard in a nice review article [60].

In both cases, the bridge bonds (E_b–E_b) are formed from almost pure p-orbitals. For the long-bond isomer **57** they are slightly polarized by s-orbital contribution furnishing a less effective orbital overlap and consequently a weak E–E bond (inverse σ-bond). The unpolarized p-orbitals of the short-bond isomer **56** form a E–E bond with slightly larger π-character although the individual orbitals are rotated by about 40° from the ideal alignment (cf. ∼30° for **57**). Recent comprehensive calculations by Koch et al. [61] for the short-bond and long-bond tetrasilabicyclo[1.1.0]butanes (Si_4R_6, with R = H, Me, Ph, 2,6-dimethylphenyl) revealed that the relative energies of **56** and **57** strongly depend on the substituent R due to a competition between ring strain [62] and steric effects (Scheme 15).

Small groups R favor the formation of **57** (larger angle Φ) while steric repulsion (larger angle Θ) provide the same isomer to be instable for bulkier aryl substituents. Hence, "true" bond-stretch isomerism can only be discussed for selected ligands of suitable size because both isomers **56** and **57** do not coexist for very small and for sterically demanding substituents (Table 1). In contrast, the germanium bicyclic structure is more flexible than the corresponding silicon isomer [63]. The difference in strain energy between four-membered and three-membered rings, which decides the preferred geometry for small groups R, is much more pronounced for the germanium rings compared to its silicon counterparts. Hence, the long-bond structure **57** is clearly favoured over **56**. For the calculated germanium analogues, Ge_4R_6, **56** revealed to be no minimum on the PES indicating that apparently only the long-bond isomer exists



Scheme 15. Tetrametallabicyclo[1.1.0]butanes of the general formula E_4R_6 (with E = Group 14 element); definition of the angles *Φ* and *Θ*.

consequently excluding bond stretch isomerism. AIM methods for the long-bond germanium as well as silicon isomer showed no bond-critical point (bcp—a saddle point in the total electron density indicating the existence of a bond between two atoms in a molecule) [64] between the bridgehead atoms and only one ring critical point. Therefore, the structure can be described as a biradical in a singlet state confirming Schleyer's original description from 1987 for the model compound Si_4H_6 [59a].

Although the quantum chemical calculations predict such interesting phenomena for some isomers of the E_4R_6 PES [65,66], synthetically accessible and structurally characterized tetrasilabicyclo[1.1.0]butanes are very rare (Scheme 16). The sterically encumbered derivative **58** reported by Masamune and co-workers [67] has a normal Si_b–Si_b bond length of 237.3 pm and an interflap angle *Φ* of 121° suggesting its classification as short-bond isomer **56**. However, the physical and chemical properties of **58** indicate the energetically close relationship to the biradicaloid form. Crystals of **58** are thermochromic and the ring-inversion barrier for **58** was estimated by NMR methods to be low ($E_a \approx 15\,\mathrm{kcal\,mol^{-1}}$). Furthermore, the central Si_b–Si_b bond is unusually reactive since degassed water or an equimolar amount of Cl_2 are readily added yielding the hydration product or the dichlorocyclotetrasilane, respectively.

Table 1
B3LYP/6-31G(d)-calculated relative energies and E_b–E_b distances and angles *Φ* and *Θ* of E_4R_6 isomers (E = Si, Ge) according to Koch et al.

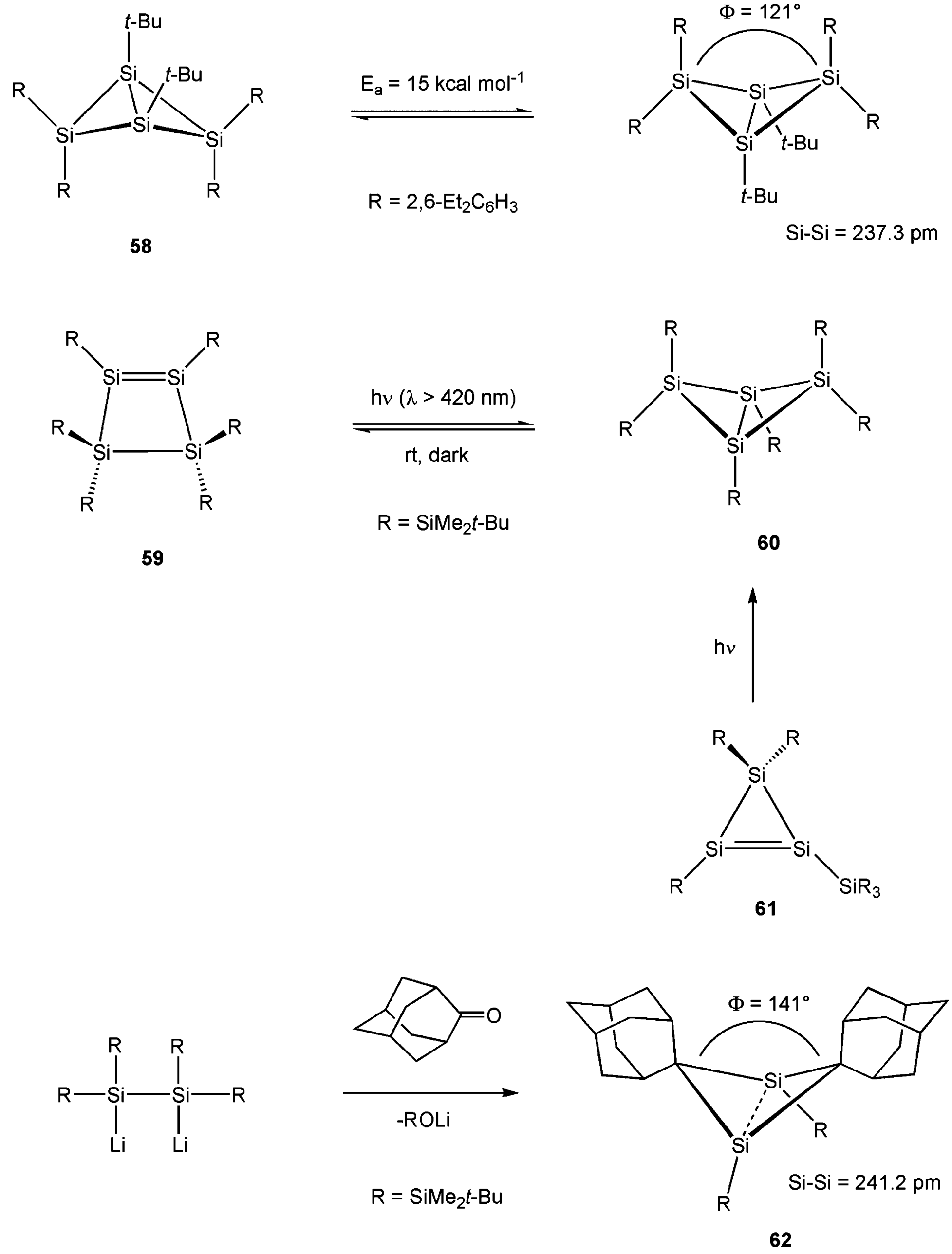
Isomer	E	Values	R = H	R = Me	R = Ph	R = DMP
56	Si	Energy ($\mathrm{kJ\,mol^{-1}}$)	–	14.9	2.3	0.0
		E_b–E_b (pm)	–	231.1	230.7	233.2
		Φ (°)	–	129.1	134.4	128.8
		Θ (°)	–	136.9	140.0	150.4
57	Si	Energy ($\mathrm{kJ\,mol^{-1}}$)	0.0	0.0	0.0	–
		E_b–E_b (pm)	286.0	286.0	286.4	–
		Φ (°)	142.2	144.7	143.6	–
		Θ (°)	92.2	103.7	110.1	–
56	Ge	Energy ($\mathrm{kJ\,mol^{-1}}$)	–	–	–	–
57	Ge	Energy ($\mathrm{kJ\,mol^{-1}}$)	0.0	0.0	0.0	0.0
		E_b–E_b (pm)	313.7	315.2	323.5	325.4
		Φ (°)	143.8	147.3	149.5	142.2
		Θ (°)	87.0	97.3	103.8	117.5

DMP = 2,6-dimethylphenyl.

A similar observation was made by Kira et al. for the silyl-substituted tetrasilabicyclo[1.1.0]butane derivative **60**, which was generated by photolysis with a high-pressure Hg arc lamp ($\lambda > 420$ nm) from the tetrasilacyclobutene derivative **59** [68]. In the photostationary state at 288 K, 91% conversion was reached, as determined by UV/vis spectroscopy. The photoproduct **60** was characterized by ^1H NMR spectroscopy and by the product analysis of hydrolysis of **60**. However, no further spectroscopic data such as ^{29}Si or ^{13}C NMR spectra were obtained for **60** because it thermally rearranges quantitatively to the cyclobutene in the dark ($k_{288} = 5.67 \times 10^{-5}\,\mathrm{s^{-1}}$). Remarkably, this isomerization cycle can be repeated more than 10 times without any signs of decomposition. Both the thermal and photochemical isomerizations were confirmed using substituent-labeling experiments to proceed via 1,2-silyl-migration rather than skeletal isomerization [69]. The cyclotrisilene **61** also isomerizes photochemically to the bicyclo[1.1.0]tetrasilane (**60**), which converts thermally to the tetrasilacyclobutene derivative **59**.

Recently, Kira et al. were able to isolate a compound (**62**) [70] featuring a long central Si_b–Si_b bond of 241.2 pm, which is considerably longer than Si–Si bonds of known disiliranes (227–233 pm). **62** was obtained as air- and moisture-sensitive bright yellow crystals in 70% isolated yield by using a formal double sila-Peterson reaction of tetrakis(*t*-butyldimethylsilyl)dilithiosilane and adamantanone. In addition to the X-ray crystal structure results, quantum chemical calculations as well as ^{13}C and ^{29}Si NMR spectroscopic investigation for the 1,3-disilabicyclo[1.1.0]butane **62** predicted this long-bond isomer to be stable in the solid-state and in solution. Whereas, the short-bond isomer **58** reported by Masamune et al. was found to show facile ring-flipping at room temperature, no such flipping was detected for **62** as evidenced by ^{13}C NMR spectroscopy. Interestingly, **62** shows a distinct band maximum at 420 nm due to the $\sigma \rightarrow \sigma^*$ transition of the Si_b–Si_b bond. The biradical nature of the Si–Si bond in **62** was confirmed by its reactions with alkylhalogenides, phenylacetylene, and ketones [71]. As shortly mentioned by Kira [71], the analogous germanium compound, 1,3-digermabicyclo[1.1.0]butane, was synthesized (73% yield) and characterized as long-bond isomer consisting of an UV/vis absorption maximum at 440 nm. However, no further data were published for this compound until now.

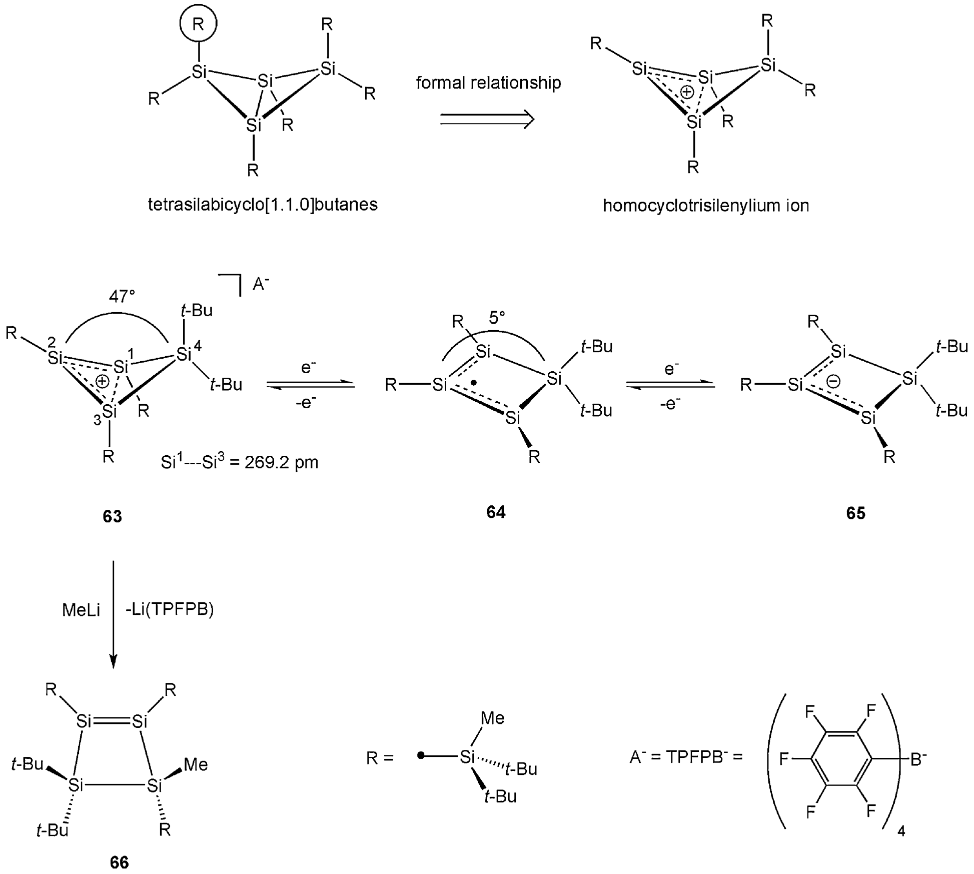
Although not discussed in the literature, one may anticipate a relationship between tetrasilabicyclo[1.1.0]butanes and homocyclotrisilenylium ions, which are formally accessible by



Scheme 16. Syntheses of tetrasilabicyclo[1.1.0]butanes (**58** and **60**) and 1,3-disilabicyclo[1.1.0]butane **62**.

removing one anionic substituent (i.e., R^-) from one “wing tip” of the bicycle (Scheme 17). In reality, homocyclotrisilenylium ions such as **63** are available by reacting silyl substituted cyclotrisilenes with $[Et_3Si(benzene)]^+$ as reported recently by Sekiguchi [72]. The X-ray structure analysis of the first free silyl cation in the solid state (**63**) revealed the four-membered ring to be folded by 47° featuring a long transannular silicon–silicon contact of 269.2 pm. This is caused by *1,3-orbital interaction* due to the homoaromatic character of **63**. Note that the cation **63** smoothly reacts with small nucleophiles such as methyllithium to produce a cyclotetrasilene derivative (**66**). The latter is directly related to the one used by Kira (**59**, *vide supra*) to photolytically generate the silyl-substituted tetrabicyclo[1.1.0]butane derivative **60** and, hence, supporting the formal relationship depicted in Scheme 17. Furthermore, as reported by Sekiguchi, the free silyl cation **63** is readily reduced to the neutral radical **64** [73] and the cyclotetrasilenide **65**; [74] the heavier congener of the latter was known from the literature by work of Weidenbruch and co-workers on cyclotetragermanide [75].

Despite of an interesting example of bond stretch isomerism and indications for biradicaloids in solid-state chemistry, which was found by Nesper for the Zintl phase Ba_3Ge_4 containing $[Ge_4]_\infty{}^{6-}$ chains [76], no other stable molecular metallabicyclobutanes of the heavier Group 14 elements have been reported to date. However, closely related dimetalla derivatives featuring considerably long central carbon–carbon bonds [77] were reported for the 2,4-disilabicyclo[1.1.0]butane **67** [78] ($d_{C\text{–}C} = 178.1$ pm) and the disilabenzvalene **68** [79]



Scheme 17. Formal relationship of tetrasilabicyclo[1.1.0]butanes to homocyclotrisilenyl ions (top); reduction of the silyl cation (**63**) to the neutral radical (**64**) and the cyclotetrasilenide (**65**); the cation reacts with MeLi furnishing a cyclotetrasilene **66**, a derivative of **59** which was used by Kira and co-workers to photochemically generate the bicyclo[1.1.0]butane **60** (see Scheme 16).

($d_{C–C}$ = 168.0 pm). Furthermore, West and Driess [80] reported on 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes (**69**) and the corresponding As compounds **70** (Scheme 18). Both Group 15 element bicycles contain unusually long P–P (ca. 238 pm versus 220–223 pm in normal diphosphanes) and As–As (260 pm compared to ∼244 pm for normal As–As single bonds).

As mentioned by Driess et al. [81], the P_2Si_2 butterfly-like compounds of the type **69** also tend to undergo a ring inversion via an unusual silanediyl fragmentation in the transition state, although the ring inversion barrier for $(H_2Si)_2P_2$ was predicted to be relatively high (51.0 kcal mol^{-1} (MP2); cf. −40 to 50 kcal mol^{-1} for **5**). The authors excluded a biradical character on the basis of orbital occupation numbers (CAS-MCSCF/6-31G*) and singlet–triplet gaps ($\Delta E_{S-T} = -88.4$ kcal mol^{-1}). The weak P–P bond was attributed to ring strain and repulsion between the two negatively charged P atoms (σ-effect of the Si^+–P^- polarized bonds). However, as was shown by the recent calculation on bond stretch isomerism and its strong dependence on the substituent R mentioned above, such systems may be an interesting target for (re)investigations in the future.

4.2. *[1.1.1]Propellanes E_5R_6 and related compounds*

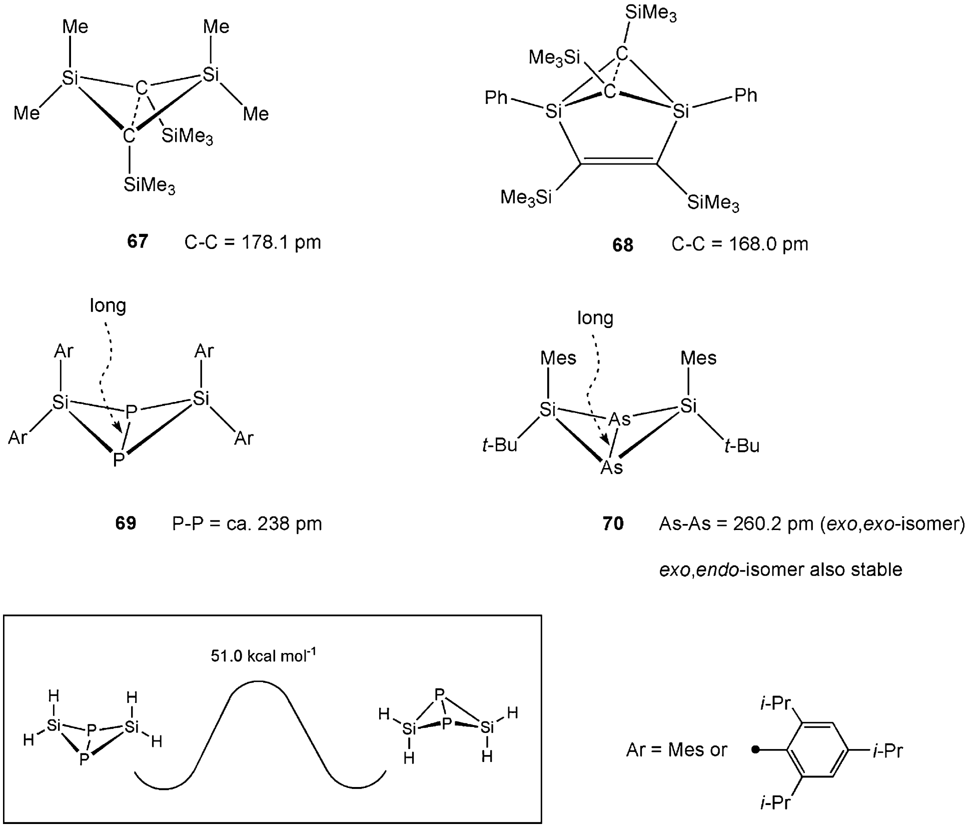
As one might expect, when the intrinsic σ-bond strength is weakened by taking an element from a higher period and the number of annulated three-membered rings is increased, the open biradicaloid form is stabilized even more. As in the [1.1.0]bicyclobutanes, the central bond between the bridgehead atoms of [1.1.1]propellanes is significantly elongated. This was impressively demonstrated by Sita and Kinoshita in the early 1990s who succeeded in isolating the pentastanna[1.1.1]propellane Sn_5R_6 **71** and the derivative Sn_7R_8 **72** (with R = 2,6-$Et_2C_6H_3$) from the reduction of the cyclotristannane with lithium metal in THF (Scheme 19) [82]. Although the number of substituents exceeds the number of tin atoms, the compounds contain two unsubstituted tin atoms [83]. The experimental determined distances between the bridgehead tin atoms are 20% longer than a regular tin–tin single bond. That **71** and **72** have considerable singlet biradicaloid character is further corroborated by their electrochemical behavior. Cyclic voltammetry of both compounds revealed two quasi-reversible one-electron reduction waves (Eqs. (2a), (2b), (3a) and (3b).

$$Sn_5R_6\,(\mathbf{71}) + e^- \rightarrow [Sn_5R_6]^-\,(\mathbf{73})$$

$$E^0_{1/2,\mathrm{NHE}} = -1.41\,\mathrm{V} \tag{2a}$$

$$[Sn_5R_6]^-\,(\mathbf{73}) + e^- \rightarrow [Sn_5R_6]^{2-}\,(\mathbf{75})$$

$$E^0_{1/2,\mathrm{NHE}} = -1.93\,\mathrm{V} \tag{2b}$$



Scheme 18. Related bicyclobutanes consisting of long central carbon–carbon bonds (**67** and **68**, top); 1,3-diphospha- (**69**) and 1,3-diarsa-2,4-disilabicyclo-[1.1.0]butanes (**70**) with unusually long E–E bonds.

$$\mathrm{Sn_7R_8}\ (\mathbf{72}) + \mathrm{e^-} \rightarrow [\mathrm{Sn_7R_8}]^-\ (\mathbf{74})$$

$$E^0_{1/2,\mathrm{NHE}} = -1.35\,\mathrm{V} \tag{3a}$$

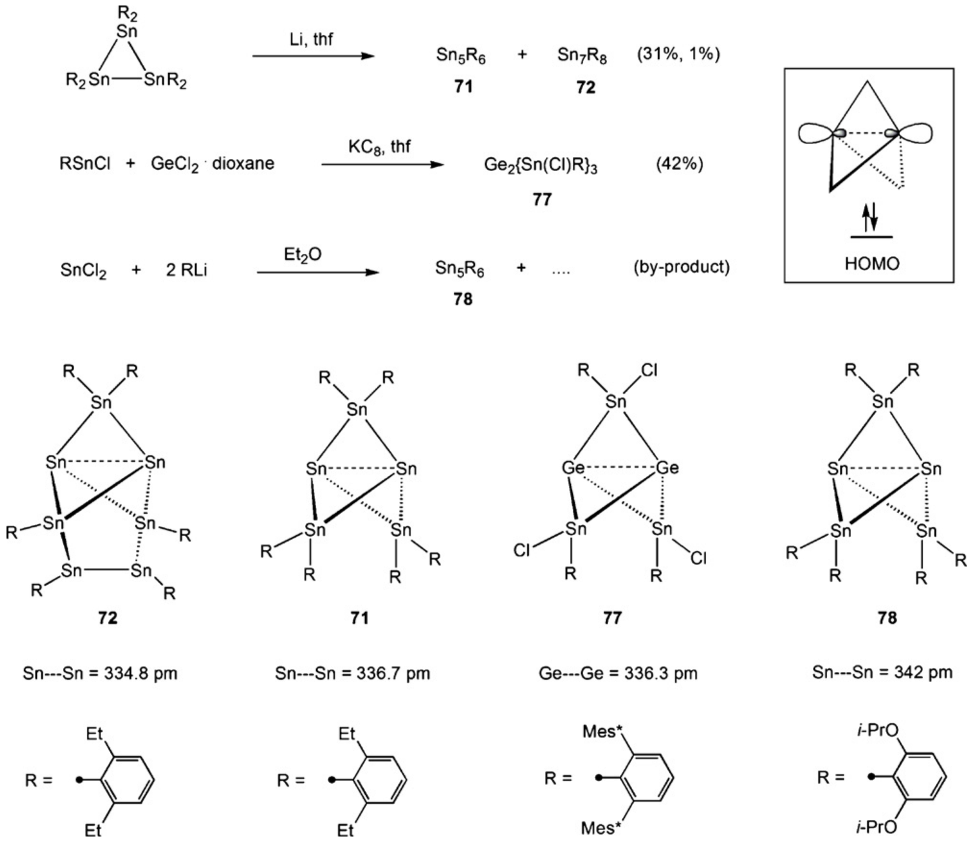
$$[\mathrm{Sn_7R_8}]^-\ (\mathbf{74}) + \mathrm{e^-} \rightarrow [\mathrm{Sn_7R_8}]^{2-}\ (\mathbf{76})$$

$$E^0_{1/2,\mathrm{NHE}} = -1.90\,\mathrm{V} \tag{3b}$$

Thus, both compounds can be reduced stepwise to give the radical anions **73** and **74** and the dianions **75** and **76**, respectively. The formally electron-deficient bridgehead tin centres (seven valence electrons) are converted into eight-valence-electron-configurated $(\mathrm{SnR_2})_3\mathrm{Sn}^-$ entities.

Although not studied in detail with regard to their electrochemical properties, similar compounds such as $\mathrm{Sn_5R_6}$ **78** (R = 2,6-(O*i*-Pr)$_2$C$_6$H$_3$) and Ge$_2${Sn(Cl)R}$_3$ **77** (R = 2,6-Mes$_2$C$_6$H$_3$) were reported recently by Drost et al. [84] and Power and co-workers [85], respectively. Remarkably, the distance between the bridgehead germanium atoms in **77** (336.3 pm) is similar to those of the tin atoms in **71** (336.7 pm) and **72** (334.8 pm). Power explained this effect on the basis of the electronegative Cl substituents on the bridging tin moieties. Despite the large aryl ligands, the C–Sn–Cl angle (103.8°) is less than the average C–Sn–C angle in **77**. The reduction of the angle between the tin substituents leads in turn to a wider Ge–Sn–Ge angle and thus a greater Ge–Ge separation. The lengthened Sn–Sn bridgehead separation reported by Drost for **78** (342 pm), featuring a more electron-withdrawing aryl substituent compared to **77**, is also in accord with this description. The comparison of the structural data for these metalla[1.1.1]propellanes impressively confirms that the distance between bridgehead atoms can be systematically varied by changing the constituent atoms of the cluster and their substituents. Thus, a substituent depended control over the degree of interactions – and therefore the amount of biradical character in these systems – may be anticipated.

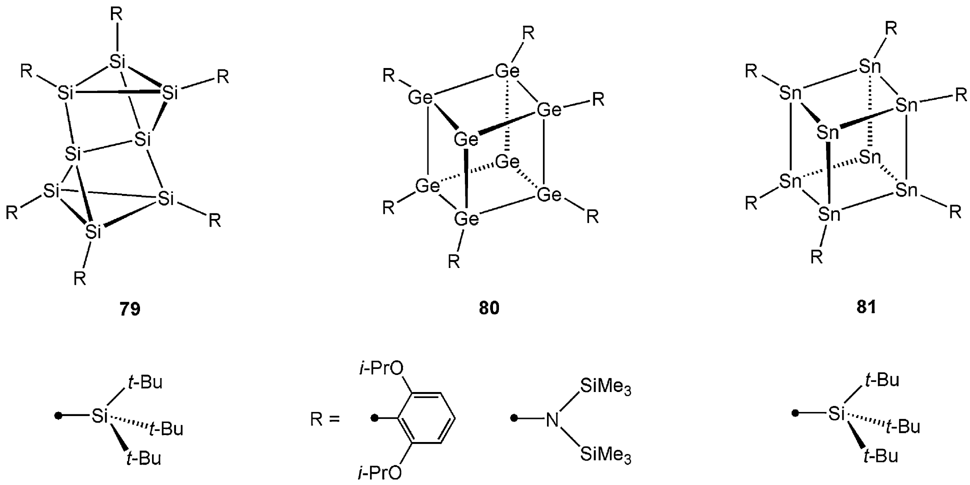
In this context it is important to note that Wiberg and co-workers as well as Schnepf et al. performed work on silicon [86], germanium [87], and tin [88] clusters of the general formula [E$_8$R$_6$] (**79**–**81** in Scheme 20). The recently reported silicon compound **79** bears a Si$_2$ dumbbell ($d_{\mathrm{Si-Si}}$ = 229(1) pm) with “inverted tetrahedrally” coordinated Si atoms within its molecular core, whereas, the corresponding Ge (**80**) and Sn (**81**) clusters consist of two unsubstituted or “naked” Group 14 element atoms [83]. Although the origin of the structural differences remains to be answered, the silicon cluster may formally adopt the analogous hexahedral structure of the heavier congeners by stretching of the Si$_2$ bond. A comparison of the bonding situation in the differently substituted germanium clusters **80** (with R = 2,6-(O*i*-Pr)$_2$C$_6$H$_3$ or N(SiMe$_3$)$_2$) revealed that the ligand R is not only of importance for a protection of the cluster framework but also has a strong influence on the bonding situation within the core. As shortly mentioned by Schnepf et al., these compounds may formally be described as biradicals. As the Ge· · ·Ge separation between the unsubstituted germanium atoms is much larger (e.g.,



Scheme 19. Syntheses of [1.1.1]propellanes of the heavier Group 14 elements; experimentally found $E_b\cdots E_b$ separations between the bridgehead atoms.

518 pm for **80** with R = N(SiMe$_3$)$_2$) than in the [1.1.1]propellane systems described above, a triplet ground state may be anticipated. However, the EPR spectrum of **80** (with R = N(SiMe$_3$)$_2$) shows no signal and quantum chemical calculations performed by Schnepf et al. predicted the singlet state to be more stable than the triplet ($\Delta E_{S\text{–}T} = -23$ kcal mol^{-1}).

The question about the interactions between the bridgehead atoms of metallapropellanes has been extensively discussed in the literature [89–91] (Table 2). Even the simplest [1.1.1]propellane system of the Group 14, the all-carbon propellane C_5R_6 **82** (M = C) – although thoroughly described from both experimentalists and theoreticians – has attracted renewed interest [92]. All efforts are mainly driven in order to answer the central issue concerning the nature of the interaction between the “inverted” bridgehead atoms. As can be seen from the schematic HOMO and LUMO representation (Scheme 21) the former is bonding and the latter is anti-bonding with respect to the C_b–C_b distance. It was found that C_5H_6 has a low-lying triplet state due to its inverted C_b–C_b bond. Low-energy electron impact spectroscopy determined the vertical excitation energy to the lowest triplet state to be 4.70 eV ($\Delta E_{S\text{–}T} = -108.4$ kcal mol^{-1}; calculated: -107.1 kcal mol^{-1} (U)B3LYP/cc-pVTZ) [93]. Recent



Scheme 20. Group 14 element cluster compounds of the general formula [E_8R_6] (with E = Sn, Ge).

Table 2
Structural parameters for calculated Group 14 metallapropellanes, bicyclopropanes, and their derivatives

M	M_5H_6 (**82**) [99]	M_5H_8 (**83**) [99]	Δd^{a}	M_2O_3 (**84**) [100] [b]	$H_2M_2O_3$ (**85**) [100] [b]	Δd	M_2S_3 (**86**) [100]	$H_2M_2S_3$ (**87**) [100]	Δd	$M_2(CH_2)_3{}^{c}$ (**88**) [101]	$H_2M_2(CH_2)_3$ (**89**) [101]	Δd
C												
d_c	162.5	188.3	25.8	151.1	162.2	11.1	164.0	202.0	38.0	159.6	187.5	27.9
d_p	152.3	155.5		140.8	142.7		179.2	184.6		151.7	155.0	
Si												
d_c	279.3^{d}	292.5	13.2	207.6	206.0	−1.6	236.3	237.3	1.0	229.1	229.3	0.2
d_p	235.8^{c}	236.8		170.7	170.0		218.0	218.1		192.3	191.0	
Ge												
d_c	299.1	305.3	6.2	225.0	222.5	−2.5	–	–	–	247.0	247.1	0.1
d_p	248.8	247.7		180.6	179.5		–	–		202.8	200.7	
Sn												
d_c	346.9	350.9	4.0	257.7	254.6	−3.1	–	–	–	280.2	278.5	−1.7
d_p	285.7	284.0		198.5	197.1		–	–		223.0	220.2	

Values in pm; details concerning the level of theory can be found in the literature citations.

[a] $\Delta d = d_c(\text{bicyclopentane}) - d_c(\text{propellane})$ (pm).

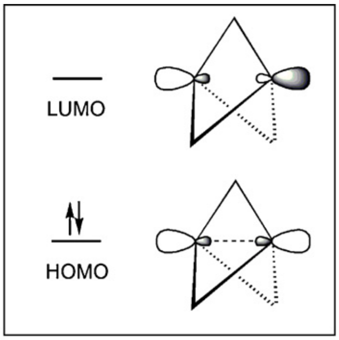
[b] See also Ref. [98].

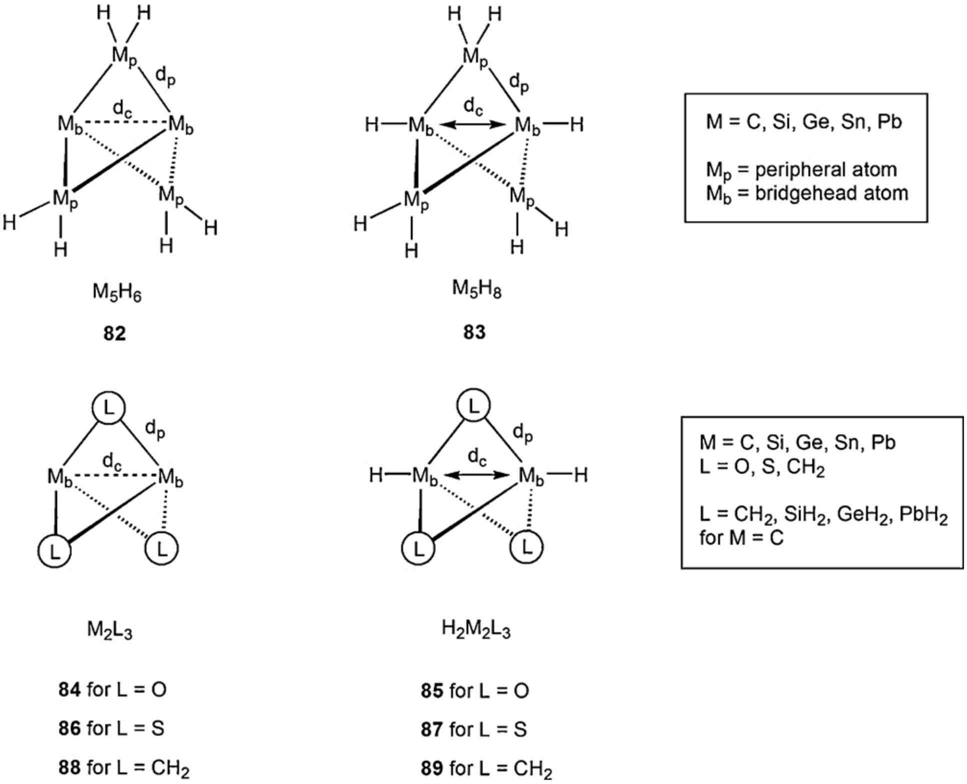
[c] ΔE_{S-T} for M = Si, Ge, and Sn between 55.8 and 47.1 kcal mol^{-1}.

[d] See also Ref. [96].

experimental investigations on the electron density in an all-carbon [1.1.1]propellane derivative as well quantum chemical calculations performed by Luger and co-workers revealed the existence of a bonding path between both bridgehead carbon atoms [94]. The authors found significant electron density at the bond critical point from which a bond order of 0.71 was deduced. However, the corresponding experimentally observed Laplacian at the bcp is positive (even larger than the calculated one) [95] suggesting non-covalent interactions between the bridgehead atoms. Nevertheless, the central C_b–C_b contact (d_c) in the propellane **82** is only slightly longer than the peripheral carbon–carbon bonds (d_p) and significantly shorter than d_c in the bicyclic structure of C_5H_8 (**83**). For the heavier congeners the differences (Δd) between $M_b\cdots M_b$ in **82** and those in the corresponding bicycle **83** are much smaller than for M = C ($\Delta d = 25.8$ pm), especially when the inherently larger metal distances are taken into account. The calculated differences Δd decrease upon descending the Group 14 with values of 13.2, 6.2, and 4.0 pm for M = Si, Ge, and Sn, respectively. Quantum chemical calculations of Schleyer and Janoschek concerning the pentasila[1.1.1]propellane (M = Si) suggested substantial singlet biradical character and that "*it would be misleading to represent the structure by drawing a line between the bridgehead atoms*" [96]. Schoeller et al. has also predicted a long $Si_b\cdots Si_b$ separation in the pentasila compound [97]. Nagase has presented evidence which supports the existence of a chemical bond, i.e., the overlap between the orbitals forming the central M–M bonds for Si, Ge, and Sn is comparable to that for the C–C bond in the parent [1.1.1]propellane [98]. He described the biradical character of the Sn···Sn interaction in **82** as very small and comparable to that of the carbon homologue. On the other hand, Gorden and co-workers [99,100] pointed out that the similarity of the $M_b\cdots M_b$ distances in **82** and **83** (for M = Ge and Sn) puts in doubt the existence of a metal–metal bridgehead bond in metallapropellanes of the general formula **82** (with $M \neq C$). They also found that the $M_b\cdots M_b$ bonding interactions decrease on descending the group. Hence, for M = Sn, there is only a little difference Δd in the $M_b\cdots M_b$ interaction in **82** and in **83**. The natural orbital occupation numbers given by Gorden et al. suggest fairly small biradical character in the ground state [1.1.1]propellanes (with M = C, Si, Ge, Sn) consisting of a maximum biradical character of 14% for the silicon derivative, which is in accordance with Schleyer's [96] earlier assumption. Other evidence against significant $M_b\cdots M_b$ bonding is corroborated by the similarity of the d_c in the singlet and triplet states of M_5H_6 and that no bcp has been located along the M–M interaction lines for the metallapropellane systems (M = Si, Ge, Sn). But note that slight differences in the charge densities of these systems can affect the absence or presence of M_b–M_b bcp in these species. As was pointed out recently by Sandstrom and Ottosson [101], the absence of M_b–M_b bcp's may also result from reversed order of the σ(M–M) and σ^*(M–M) orbitals, so that the latter becomes the HOMO for metallapropellanes with M = Si, Ge, and Sn.

For hetero[1.1.1]propellane systems some interesting effects were proposed by quantum chemical calculations. For instance, Inagaki and co-workers [102,103] expected electropositive groups to increase the central carbon–carbon separation within the investigated system M_2L_3 (with M = C, L = SiH_2, GeH_2, SnH_2, PbH_2). Theoretical work of Nagase [98], Gorden and co-workers [99,100] and Sandstrom and Ottosson [101] predicted that substitution of the MH_2 groups in **82** by suitable groups L stabilize the central bond and to shorten it. Electronegative groups L lead to significantly shortened central $M_b\cdots M_b$ distances for both M_2L_3 and $M_2L_3H_2$. For L = O the metal–metal distances in **84** and **85** are very similar for M = Si to Sn and much shorter than the single bond distances in H_3M–MH_3. For instance, for M = Si the calculated silicon–silicon separation of 207.6 pm for **84** (206.0 pm for **85**) is almost identical to the experimentally determined Si≡Si triple bond distance in RSi≡SiR described by Sekiguchi (206.22(9) pm, R = –Si(*i*-





Scheme 21. [1.1.1]Propellanes M_5H_6 (**82**) and bicyclopentanes M_5H_8 (**83**) of Group 14 elements (top); hetero[1.1.1]propellanes M_2L_3 and bicyclopentanes $H_2M_2L_3$ (**84**–**89**, bottom), with d_c = distance between the central atoms M_b; d_p = distance between the central atoms M_b and the peripheral atoms M_p or L. See also Table 2 for numbering.

Pr)[CH(SiMe$_3$)$_2$]$_2$) [104]. Furthermore, for M = Ge and Sn this bond is approaching those in the corresponding germanium (228.50(6) pm) and tin (266.75(4) pm) compounds REER (E = Ge–Sn; R = –C_6H_3-2,6-Dipp$_2$ (Dipp = C_6H_3-2,6-*i*-Pr$_2$); –C_6H_3-2,6-Trip$_2$ (Trip = C_6H_2-2,4,6-*i*-Pr$_3$)) featuring bond orders of approximately 2 as described by Power and co-workers [105].

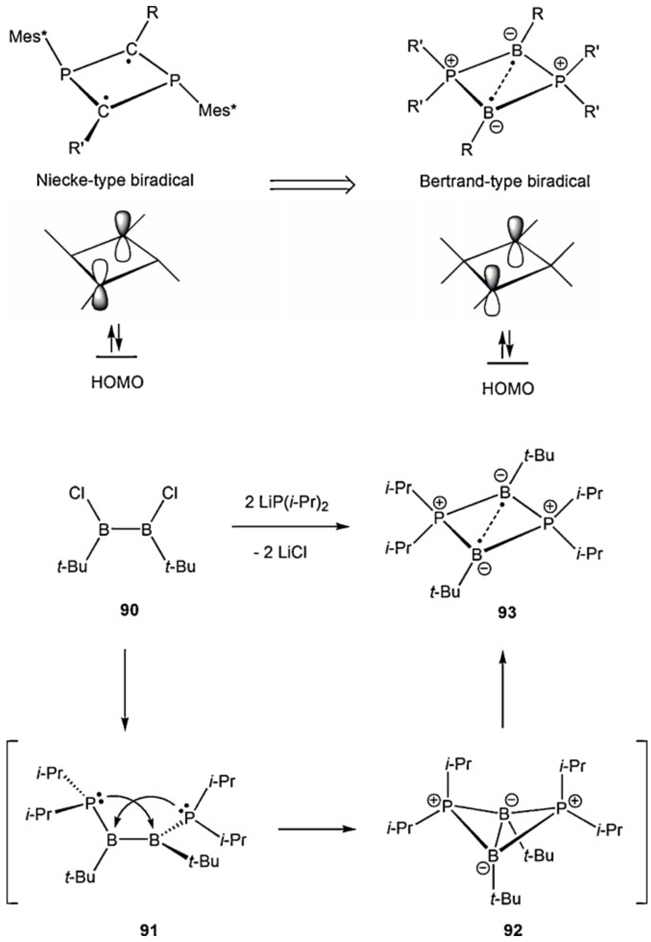
[1.1.1]Metallapropellanes may be described as donor–acceptor complexes between a central M_2 unit and three surrounding MR_2 or L groups [98]. For L = MR_2, the central M_2 entity acts as acceptor while the peripheral MH_2 units act as the donor ($[H_2M]_3 \rightarrow M_2$). The dominant electron donation into the π^*-orbital of the original M_2 unit is responsible for the stretching of the central M–M bond. When the peripheral ligands are more electronegative, e.g., CH_2 or O, the bridgehead atoms become the donors and consequently the central bond is shortened ($M_2 \rightarrow L_3$). Nagase suggested that a π-complex between M_2 and three oxygen groups (L = O) results in three 3-center-2-electron bonds and that the electron density distribution of the bond path adopts a T-shaped structure. In contrast, Gordon and co-workers found no support for the T-shaped bonding description. In their view, the short M–M distances in the trioxa[1.1.1]propellanes and in the bicyclic analogues could result simply from geometrical constrains. Furthermore, Gordon concluded that the unusually short bridgehead distances in both M_2O_3 (**84**) (or M_2S_3, **86**) and $M_2O_3H_2$ (**85**) (or $H_2M_2S_3$, **87**) do not result in significant bonding interaction and despite the short $M_b\cdots M_b$ distances these compounds (with M = Si, Ge, Sn) possess a considerable degree of biradical character.

The general conclusion from the discussion above is that shorter $M_b\cdots M_b$ distances do not necessarily correspond to bonding interactions and likewise bonding interactions can occur between atoms separated by long internuclear distances, as in [1.1.1]metallapropellanes.

5. Boron–phosphorus-based compounds

5.1. Syntheses of Bertrand-type biradicals

Boron-centered [106] singlet biradicaloids have become a new class of compounds of high interest since the pioneering work of Bertrand and co-workers in 2002 [107]. They succeeded in synthesizing and characterizing the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl (**93**), which is indefinitely stable at room temperature. The $(RP)_2(CR)_2$ motif of the Niecke radicals was replaced by the isoelectronic $(R_2P)_2(BR)_2$ unit, both containing 22 valence electrons for R = H. This had two important consequences for the stability and favorability of the open, biradical(oid) form: (1) the contribution of the resonance structure **B** (Scheme 8) to the electronic ground state is largely diminished because the P lone pair of Niecke-type compounds has been transformed into a P–C σ-bond in the Bertrand-type biradicaloids; (2) the heterocycle in **93** is expanded because of the intrinsically longer P–B bonds (~190 pm as compared to ~175 pm for P–C in the Niecke biradicals). Note that the symmetry of the HOMO (Scheme 22) allows (a net) transannular, through-space B–B π-interaction (dotted line between the boron atoms).



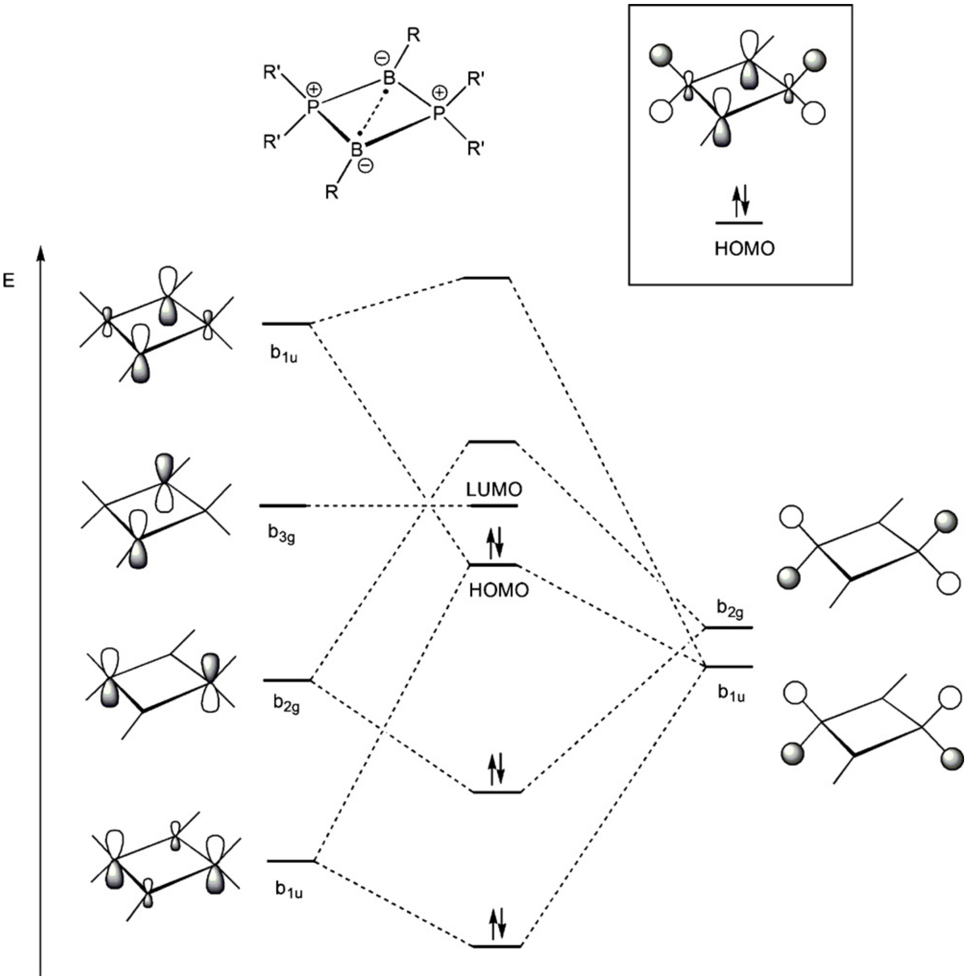
Scheme 22. Synthesis of the Bertrand biradical **93** and likely intermediates in brackets.

The synthesis of **93** proved to be simple: a clean reaction occurred when the dichlorodiborane(4) **90** was treated with two equiv. of lithium diisopropylphosphide ($LiP(i\text{-}Pr)_2$) in ethereal solvents at −78 °C furnishing **93** as extremely air-sensitive but thermally stable yellow crystals (m.p. 212 °C) in 68% yield. The X-ray crystal structure analysis revealed a perfectly planar B_2P_2 ring in which the transannular B–B distance of 257 pm is 38% longer than the longest B–B bond reported so far. Although the mechanism of the formation of **93** is not known in detail, it can be assumed that the 1,2-diphosphanyldiborane(4) **91** should be one of the initial reaction intermediates. This structure should rapidly rearrange into the 1,3-diphospha-2,4-diborabicyclo[1.1.0]butane **92** which springs apart due to steric reasons to give **93**. In other words, the choice of the sterically demanding substituents attached to P that can comfortably accommodated in the planar form of **93** allowed the crystallization of a strictly isoelectronic and isostructural transition state analogue for the bicyclo[1.1.0]butane inversion. The absence of a signal in the EPR spectrum, both in solution and in the solid state from −80 °C to room temperature, indicated that **93** has a singlet ground state. Quantum chemical calculations predicted the singlet state of **93** to be 17.2 kcal mol^{-1} ($-\Delta E_{S-T}$) lower in energy than the triplet state demonstrating a coupling between the two radical sites by through-bond and through-space B–B interactions.

Shortly after Bertrand and co-workers published the 1,3-dibora-2,4-diphosphonio-cyclobutane-1,3-diyl **93**, numerous quantum chemical calculations were reported independently by the groups of Schoeller et al. [108], Jung and Head-Gordon [109,110], Cramer and co-workers [111], and Cheng and Hu [112]. Details concerning the calculated geometries, singlet–triplet splitting (ΔE_{S-T}) and LUMO occupation numbers (if available) are compiled in Scheme 23 and Tables 3 and 4.

Cramer and co-workers suggested, beside the commonly used resonance structures that may be drawn for **93**, i.e., the open four-membered ring structure featuring one formally unpaired electron on each B atom (**93**) and the closed-shell bicyclo[1.1.0]butane (**92**), an alternative formulation. According to the authors, mixing of the out-of-plane boron p-orbitals with appropriate σ_{PR} and σ^*_{PR} orbitals may create the equivalent of an aromatic π-system. Spin-pairing in such delocalized hybrid orbitals will contribute to closed-shell character. This orbital picture is illustrated in Scheme 23 where four π-orbitals of the 1,3-diphospha-2,4-diborete ring combine with two symmetry-adapted orbitals of π-like symmetry of the P substituent [113]. Note that the HOMO is dominated by a cross-ring B–B π-bonding interaction, while the LUMO, which by symmetry cannot mix with the σ_{PR} and σ^*_{PR} combination orbitals, is B–B π^*-anti-bonding.

From the LUMO occupation numbers and the ΔE_{S-T} values given in Tables 3 and 4 the theoreticians concluded (relatively concordantly) that the biradical character of the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl compounds is not very large—far less than most other well-known organic biradicals, although still much more than normal closed-shell molecules.



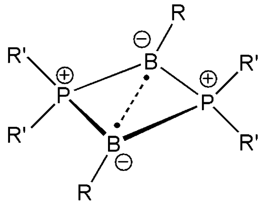
Scheme 23. MO diagram of the mixing of 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl π orbitals (in D_{2h} symmetry) with symmetry-adapted substituent orbitals on P (e.g., 1s orbital for R = H or sp^3 orbitals for R = alkyl or silyl). The figure was adapted from Cramer and co-workers in Angew. Chem. 114 (2002) 4050 [111].

The origin of the comparably low biradical character was attributed to transannular through-space interactions between the two boron atoms as well as through-bond neighboring group interactions. Upon modifying the ring constituents, the originally small gap between HOMO and LUMO for "classical" organic biradicals such as cyclobutanediyls (**5**) is increased by stabilizing the HOMO. This can roughly be explained as follows.

The initially degenerate p-orbitals that are centered on the two radical sites in the 1,3-positions can interact to form bonding and anti-bonding MOs. Due to a larger B···B distance (and larger B–P bond lengths) as compared to the C···C distance in **5**, this overlap is less effective for the Bertrand-type biradicals. The initial splitting of Φ_{R1} and Φ_{R2} is much smaller. One pair of bonding and anti-bonding orbitals of the bridging groups (Φ_{br1} and Φ_{br2}) can mix with the symmetrical combination (Φ_{R1}) furnishing a larger HOMO–LUMO gap as compared to **5**. Thus, the relative strength of through-space as well as through-bond interaction determines the final HOMO–LUMO gap and, hence, the extent of biradical character (Fig. 2). Note that, depending on aspects of energy and symmetry (cf. different orbitals Φ_{br1} and Φ_{br2} for Niecke-type biradicals) the overall ordering of HOMO and LUMO can also be reversed, like in the Niecke-type biradicals (Scheme 24) [114].

Due to this strong influence of neighboring groups (constituents or substituents) several derivatives were calculated expecting substantial changes of the overall electronic structure in dependence of the ligands employed. Indeed, as briefly mentioned by Head-Gordon, substitution of isopropyl with the more electropositive trimethylsilyl groups at phosphorus should increase the LUMO occupation number to 0.30 e^- (instead of 0.17 e^- for **93**). Cramer calculated for this alkyl to silyl replacement a substantial decrease of the singlet–triplet gap (ΔE_{S-T} (t-BuB)$_2$[(Me$_3$Si)$_2$P]$_2$) = −8.7 kcal mol^{-1}, cf. (ΔE_{S-T} (t-BuB)$_2$(i-Pr$_2$P)$_2$) = −23.4 kcal mol^{-1}). In addition, time-dependent calculations (B3LYP/6-311 + G(d,p)) predicted a UV/vis absorption of 704 nm—at much longer wavelength than found for **93** (λ_{max} = 446 nm). The ring geometry changes substantially upon silyl substitution. The P–B bonds lengthen and the B–P–B angle shrink which causes a decrease in the transannular boron–boron distance. Based on the MO-picture above given by Cramer (Scheme 23), the P–B bonds lengthening can be attributed to enhanced occupation of the LUMO and diminished occupation of the HOMO. The latter is net P-B bonding, whereas, the LUMO

Table 3
Calculated distances (pm), LUMO occupation numbers and singlet–triplet splitting (ΔE_{S-T}) (kcal mol^{-1}) for calculated model compounds



R = H, *t*-Bu, SiH$_3$

R' = H, Me, Et, *i*-Pr, SiH$_3$, SiMe$_3$

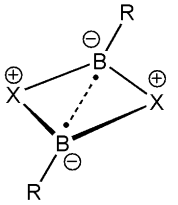
R	R′	*d*(B···B) (pm)	*d*(B–P) (pm)	LUMO occupation number (e$^-$)	($-\Delta E_{S-T}$) (kcal mol^{-1})	Reference
H	H	260.2	191.5	0.221	27.3	[109,110]
		256.0	188.8	0.233	25.8	[112]
		n.a.	191.3	n.a.	15.8[a]	[108]
		n.a.	188.8	0.21	18.7	[111]
		258	191	n.a.	17.2	[107]
H	Me	n.a.	188.7	0.21	20.1	[111]
H	*i*-Pr	n.a.	189.2	0.20	20.7	[111]
H	SiH$_3$	n.a.	190.5	0.39	5.8	[111]
t-Bu	H	259.0	189.4	n.a.[b]	30.4	[112]
t-Bu	Me	258.5	189.5	n.a.[b]	29.4	[112]
t-Bu	Et	258.6	190.2	n.a.[b]	27.9	[112]
t-Bu	SiMe$_3$	n.a.	193.2	0.30	8.7	[111]
SiH$_3$	H	261.1	189.8	n.a.[b]	18.4	[112]
t-Bu	*i*-Pr	n.a.	n.a.	0.169	33.7	[109,110]
		258.7	191.0	n.a.[b]	28.4	[112]
		n.a.	190.7	0.19	23.4	[111]

Details concerning the level of theory can be found in the literature citations.

[a] The authors supplied several values for various levels of theory. The MCSCF values with zero-point vibrational correction are given here. The reader is referred to the reference for detailed information.

[b] Although no LUMO occupation numbers were given, the authors supplied the number of effectively unpaired electrons from CAS(2,2)/6-31G* computations. For comparison, these values are not given. The reader is referred to the corresponding reference.

Table 4
Calculated distances (pm), LUMO occupation numbers and singlet–triplet splitting (ΔE_{S-T}) (kcal mol^{-1}) for calculated hetero-substituted model compounds



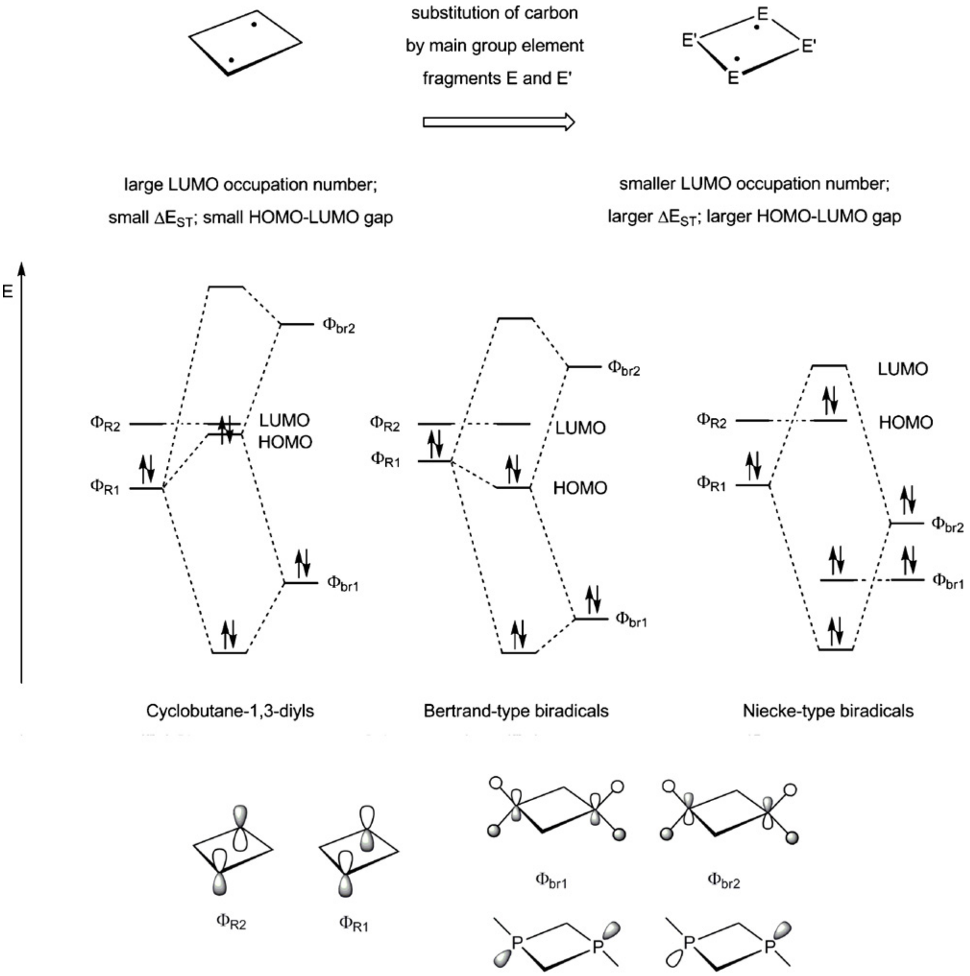
R = H

X = NH$_2$, AsH$_2$, OH, SH

R	X	*d*(B···B) (pm)	*d*(B–X) (pm)	LUMO occupation number (e$^-$)	($-\Delta E_{S-T}$) (kcal mol^{-1})	Reference
H	NH$_2$	203.8	158.0	0.437	13.1	[109,110]
H	NH$_2$	n.a.	157.0	n.a.	7.6[a]	[108]
H	AsH$_2$	n.a.	201.8	n.a.	17.0[a]	[108]
H	SH	284	n.a.	0.316	n.a.	[109,110]
H	OH	225	n.a.	0.533	n.a.	[109,110]

Details concerning the level of theory can be found in the literature citations.

[a] The authors supplied values for various levels of theory. The MCSCF values with zero-point vibrational correction are given here. The reader is referred to the reference for detailed information.



Scheme 24. Orbital interaction diagrams for three selected biradical(oid)s: Cyclobutanediyls (left), Bertrand-type (middle), and Niecke-type biradicals (right). Depending on different effects (transannular through-space interactions and through-bond neighboring group interactions) the initially small HOMO–LUMO gap of cyclobutanediyls (left) may be increased (middle) or the ordering may be reversed (right) upon changing the ring constituents. Φ_{R1} and Φ_{R2} are general representations of the p-orbitals carrying the two electrons ($CR^{\bullet}$, $BR^{\bullet -}$), Φ_{br1} and Φ_{br2} are those for the bridging entities (CR_2, PR_2^+, or PR). The energy scales (vertical axes) are only qualitative.

is not. In addition, P contributes more s character to its bonds with Si than those with C, thus applying more p character in its bonds to B, which also increases the P–B separation. Note that – perhaps contrary to an initial guess – the biradical character is increased for the species with minimum transannular B–B distance, i.e., between the centers formally assigned as carrying the unpaired spins in the simple biradicaloid resonance picture. The same conclusion was made by Head-Gordon and co-workers, who found the closely related nitrogen derivative $(HB)_2(H_2N)_2$ to be more biradicaloid with a shorter B–B distance of 203.8 pm (cf. 260 pm for $(HB)_2(H_2P)_2$). In principle this was confirmed by Schoeller et al. correlating the ground state (singlet versus triplet) of the fragment $[XH_2]^+$ for hetero-substituted $(HB)_2(H_2X)_2$ systems ($XH_2 = NH_2$, PH_2, and AsH_2) and the ΔE_{S-T} of the latter. Their calculations predicted for the nitrogen derivative a much smaller singlet–triplet separation. Furthermore, electronegative substituents should increase ΔE_{S-T}, which is in line with the prediction that electropositive P-silyl substituents should increase the biradical character. In addition, Hu et al. found a singlet–triplet energy gap of $\Delta E_{S-T} = -18.4\,\mathrm{kcal\,mol^{-1}}$ for B-silyl substituted systems (CAS(2,2)/6-31G*).

To summarize, the electronic interactions with neighboring groups (or substituents) markedly control the extent of biradical character, which is (alongside other effects) increased upon pushing more electron density to the ring system.

5.2. *Reactivity of Bertrand-type biradicals*

In order to shed some light on the theoretical predicted radical character as well as the radical behavior of 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls, Bertrand and co-workers put considerable experimental efforts towards a better understanding of molecules of this type. As shown in Scheme 23, the symmetry of the HOMO allows a *thermal* disrotatorial electrocyclic ring-closure (in contrast to the Niecke type biradicals). Therefore, a variation of the phosphorus and boron substituents was expected to strongly influence the ground-state structure, i.e., open biradicaloid form **93** versus bicyclic structure **92**, of the B_2P_2 system. Indeed, Bertrand and co-workers were able

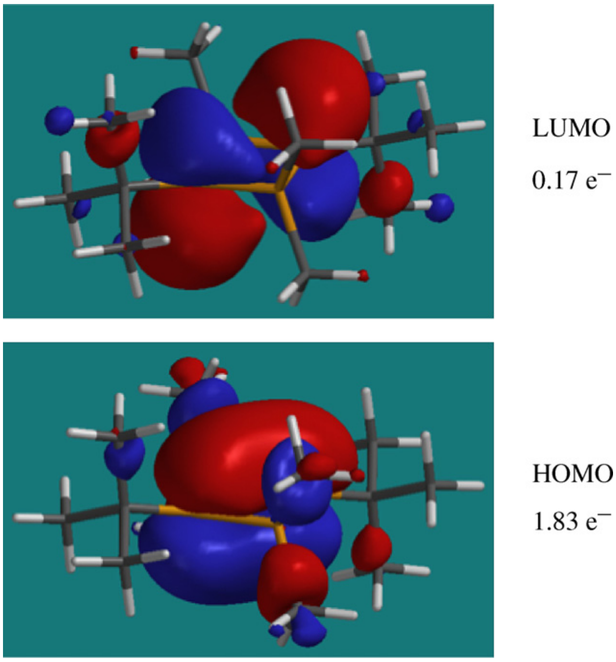
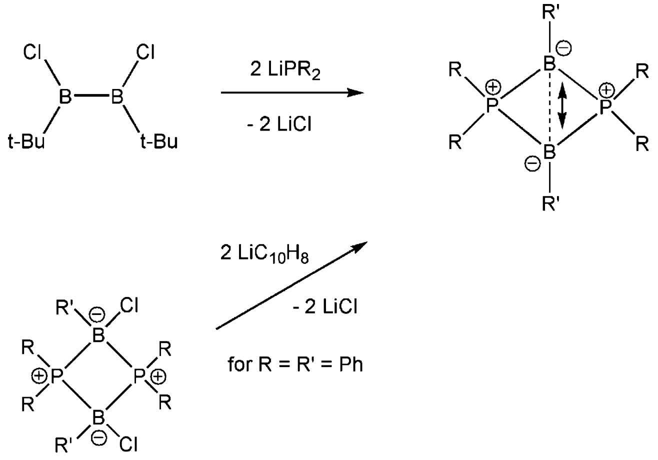


Fig. 2. Highest occupied molecular orbital (HOMO, bottom) and lowest unoccupied molecular orbital (LUMO, top) according to "perfect pairing" (PP) calculations performed by Head-Gordon and co-workers. Note that the qualitative appearance of the HOMO is the same than originally published by Bertrand et al. (Head-Gordon et al. [115a]), reproduced by permission of the PCCP Owner Societies, copyright).

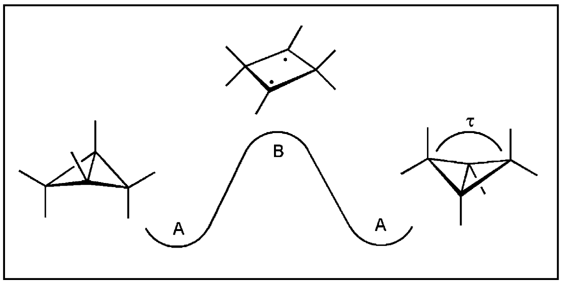
to adjust the B–B distance such that any conformation on the internal reaction profile for the bicyclo[1.1.0]butane inversion could be isolated (Scheme 25) [116].

Compounds **94**–**96** were prepared as described for **93**, derivative **97** was synthesized by the reduction of the corresponding 1,3-dichloro-1,3-diborata-2,4-diphosphoniocyclobutane with two equivalents of lithium naphthalenide ($Li^{+}C_{10}H_{8}^{\bullet -}$) in toluene. All compounds are accessible in moderate to good yield as very air-sensitive but thermally stable crystalline solids with melting points between 181 and 228 °C. Single-crystal X-ray diffraction analyses of all compounds revealed that the central B_2P_2 moiety adopt very different structures in dependence of the substituents attached to P or B. For instance, the B–B distance in the B-duryl (Dur) compound **94** is significantly shortened (224 pm, interflap angle $\tau = 130°$) compared to **93**. The most folded structure with an interflap angle of 114° was obtained for perphenylated derivative **97**, for which a normal B–B distance of 183 pm was found. Temperature-dependent NMR studies revealed that **94**–**97** invert rapidly at room temperature (equivalent axial and equatorial P-substituents on the NMR time-scale). For **96**, the inversion barrier was estimated to $\Delta G^{\neq} = 8.5\,\text{kcal mol}^{-1}$ ($T_c = -81\,°C$).

Besides this static approach that makes use of different derivatives, Mueller and Bertrand found also the first experimental evidence for the co-existence of two bond-stretch isomers in solution [117]. In the course of their systematic study on the influence of the nature of the substituents on the ground state structures of the B_2P_2 system, they prepared the B-phenyl substituted derivative ($(i\text{-}Pr_2P)_2(BPh)_2$) **98** (Scheme 26).

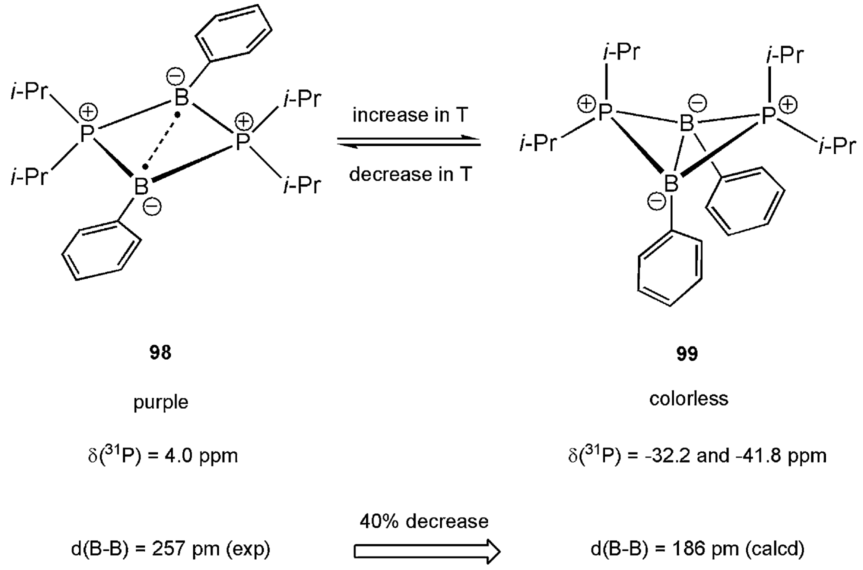


	R	R'	yield	B-B [pm]	τ [°]
93	*i*-Pr	*t*-Bu	68%	257	180
94	*i*-Pr	Dur	72%	224	130
95	Ph	*t*-Bu	71%	199	118
96	Et	Dur	58%	189	115
97	Ph	Ph	47%	183	114



Scheme 25. Synthesis of derivatives **93**–**97** (top) featuring variable B–B separations (pm) (double-sided arrow) and interflap angles τ (°); schematic representation for the reaction profile between bicyclo[1.1.0]butanes **A** and cyclobutane-1,3,-diyls **B** (bottom).

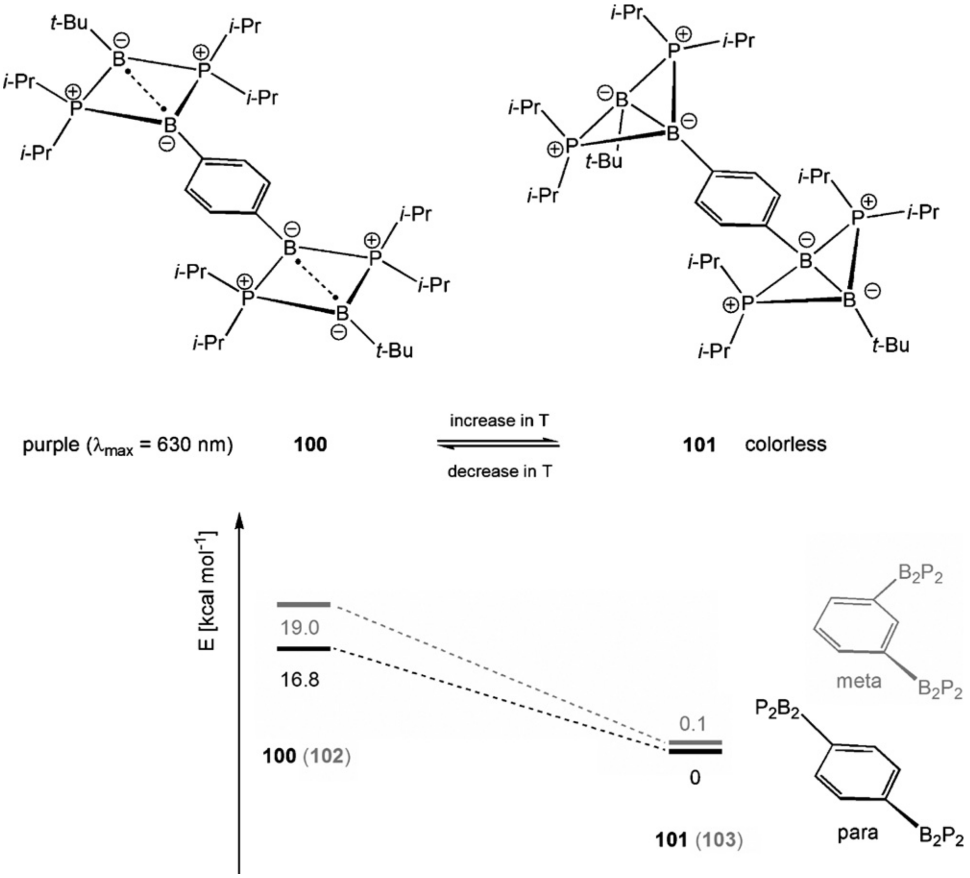
The solid state structure of ($(i\text{-}Pr_2P)_2(BPh)_2$) is similar to **93** featuring a planar, almost square B_2P_2 heterocycle (**98**) with the phenyl rings almost co-planar to the central B_2P_2 moiety and a large B–B separation of 257 pm. Temperature-dependent (30 to −145 °C) ^{31}P NMR as well as UV/vis investigations clearly showed an interconversion ($\Delta G^{\neq}_{143\,K} = 6.6 \pm 1.8\,\text{kcal mol}^{-1}$) between the open form **98** and the corresponding bicyclic isomer **99** with the latter being favored at higher temperature! Importantly, both structures coexist in solution as was proven by ^{31}P NMR spectroscopy at −145 °C ($\delta = 4.0$ ppm (**98**) and $\delta = -32.2$, −41.8 ppm (two conformers of **99**); the appearance of different conformers was supported by calculations). According to Mueller and Bertrand the order of stability of the bond-stretch isomers **98** and **99** is strongly entropy driven. The biradical isomer with the co-planar Ph groups has fewer degrees of freedom than the bicyclic isomer in which for instance the rotation around the B–C_{ipso} bond is allowed. Hence, the breaking of the σ-bond



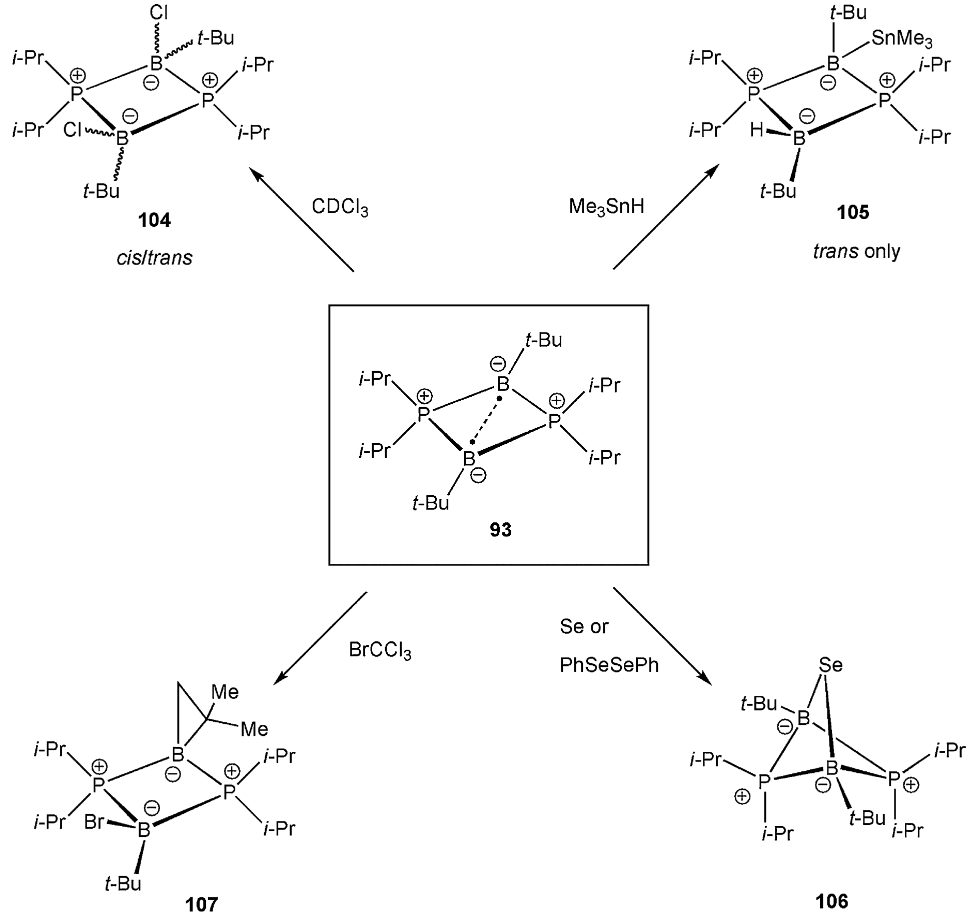
Scheme 26. Temperature dependent interconversion between a biradicaloid structure (**98**) and the corresponding bicyclic isomer (**99**).

is introduced by decreasing the temperature in opposition to the bond formation process, which is entropically favored. The same tendency was found for the *para*-phenylene-bridged structure of the intriguing tetraradicaloid **100**, featuring a bis(planar) structure in the solid state (Scheme 27) [118].

NMR and UV/vis investigations in solution revealed the deep purple, open structure **100** to predominate at low temperature, whereas, at room temperature the bis(bicyclic) system **101** is the major product. Interestingly, since the energy differences between the planar form and the bicyclic iso-



Scheme 27. Equilibrium between the *para*-phenylene-bridged tetraradicaloid **100** and the bis(bicyclic) form **101**; corresponding relative energies (kcal mol^{-1}); those for the *meta*-substituted compounds (**102** and **103**) are given in grey for comparison.



Scheme 28. Reactivity of the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl (**93**).

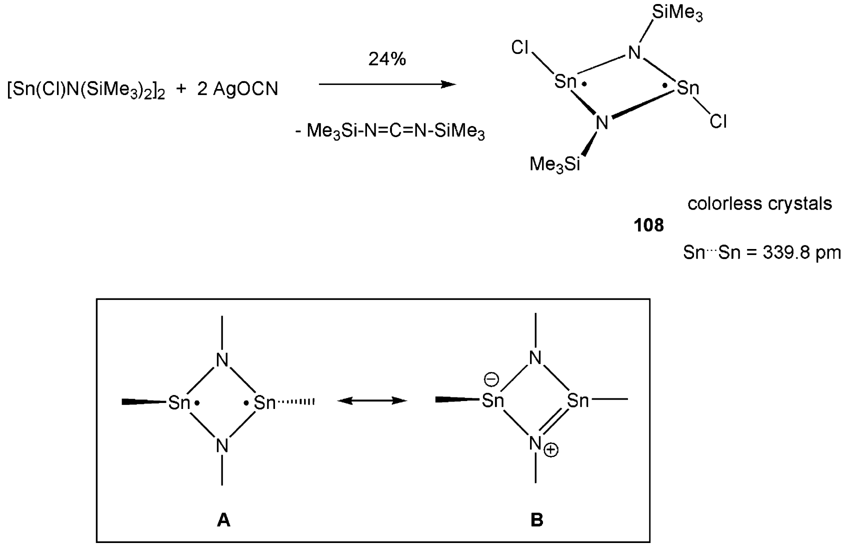
mer of substituted B_2P_2 derivatives is only a matter of a few kcal mol^{-1}, no dynamic behavior was observed for the *meta*-phenylene-bridged derivative (**102**). The latter shows the bis(bicyclic) structure in the solid state. This is confirmed by quantum chemical calculations which predicted the *para*-tetraradicaloid **100** to be 2.2 kcal mol^{-1} more stable than the *meta*-tetraradicaloid **102**, and the energy benefit for the ring closure of **100** (16.8 kcal mol^{-1}) is smaller by 2.1 kcal mol^{-1} than for **102**.

Recently, the first results concerning the chemical behavior of **93** was published by Bertrand and co-workers (Scheme 28) [119]. **93** readily reacts with mild oxidizing reagents such as chloroform yielding *cis*-**104** and *trans*-**104** in a ratio of 3:1. The B_2P_2 heterocycle remains perfectly planar for *trans*-**104** and is only slightly folded for *cis*-**104**. Through-space and through-bond B–B interaction are cancelled out and the P–B bonds are significantly elongated to 205–207 pm (cf. 189 pm for **93**). Elemental selenium as well as diphenyl diselenide cleanly react with **93** in 70% isolated yield furnishing anasterane-like structure (**106**) with long B–Se bonds and a very narrow B–Se–B angle of 71.6° at the bridging Se atom. Typical reagents for radical-type reaction such as trimethyltin hydride spontaneously react with **93** and the *trans*-1,3-adduct **105** was isolated in 73% yield featuring two signals in the ^{11}B NMR spectrum ($\delta = -3.8$ and -10 ppm). As the *trans* geometry was unambiguously deduced from single-crystal X-ray structure analysis it is likely, that a stepwise rather than a concerted mechanism is favorable for this reaction. The treatment of **93** with $BrCCl_3$ (without any radical initiator!) afforded further evidence for its radical-type behavior. Beside small amounts of the *trans*-1,3-dibromo adduct, a novel crystalline B-spiro compound (**107**) was isolated, in which the B_2P_2 four-membered ring remains intact. One boron atom is attached to a Br substituent and the second is incorporated in the BC_2 three-membered heterocycle. Although the detailed mechanism of the reaction remains the subject of speculation, **107** presumably results from a stepwise reaction, that is, (a) $Br^{\bullet}$ abstraction from $BrCCl_3$ and (b) disproportionation of the resulting radical pair to give **107** and $HCCl_3$. Especially the latter reaction product nicely demonstrate that the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls consist of (some) radical-type behavior [19].

6. Group 14 element nitrogen-based systems and related compounds

6.1. Tin or germanium centered biradicals E_2N_2

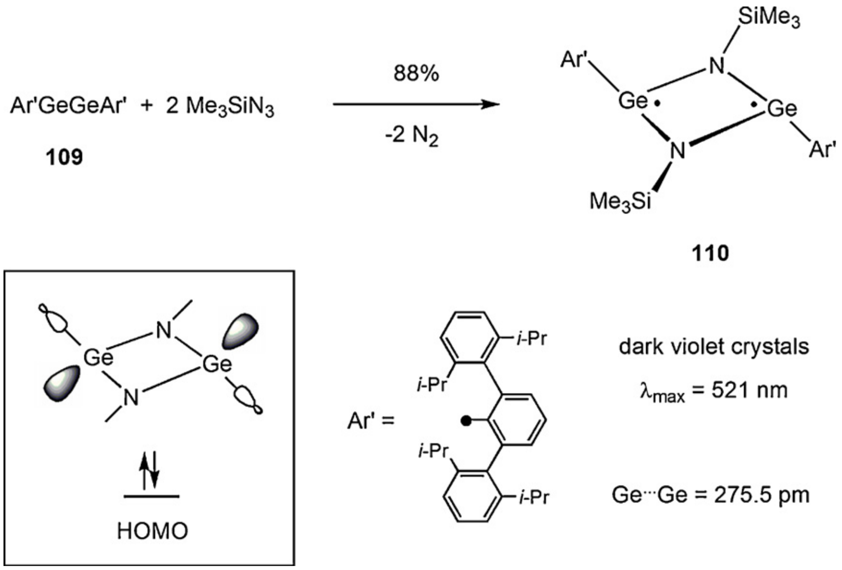
The first alternating heteroatom analogue of a cyclobuta-1,3-dienediide featuring a 5p-block element was recently communi-



Scheme 29. Synthesis of 1,3-diaza-2,4-distannacyclobutanediyl **108** according to Cox and Lappert.

cated by Cox and Lappert [120]. Colorless, diamagnetic (EPR investigations for $T = 4$–$298\,\mathrm{K}$) crystals of $(\mathrm{ClSn})_2(\mathrm{NSiMe_3})_2$ (**108**) were isolated in moderate yield in an unusual (and unexpected) reaction of dimeric $[\mathrm{Sn(Cl)N(SiMe_3)_2}]_2$ with AgOCN (Scheme 29).

The authors attribute the driving force of the reaction to the oxophilicity of silicon. An initial adduct formation of $(\mathrm{Me_3Si})_2\mathrm{N(Cl)Sn} \rightarrow \mathrm{AgOCN}$ presumably leads to a redox-reaction, yielding $\mathrm{Me_3SiN{=}C{=}NSiMe_3}$ and $[\mathrm{Sn(Cl)}\{\mathrm{NSiMe_3}\}]$, which dimerizes to **108**, Ag, and $\mathrm{Me_3SiOCN}$. The latter is believed to be transformed in $\mathrm{Me_3SiN{=}C{=}NSiMe_3}$ and $\mathrm{CO_2}$. CP-MAS ^{119}Sn NMR revealed a chemical shift of $\delta = -17$ ppm. In solution, the ^{119}Sn NMR resonance for **108** is strongly solvent-dependent and is found between −84 ppm ($\mathrm{C_6D_6}$) and −285 ppm (HMPA, toluene, $\mathrm{C_6D_6}$). This clearly indicates a nucleus, which is more shielded compared to the solid-state and in a region expected for tin at higher connectivity sites, suggesting the solvent to interact with the tin centres. In the solid-state, a planar centrosymmetric four-membered $\mathrm{Sn_2N_2}$ heterocycle was found with the nitrogen atoms slightly pyramidalized and the chlorine substituents arranged in a *trans* fashion. The transannular Sn···Sn separation of 339.8 pm seems to be of non-bonding type (cf. 280 pm in grey tin or 282 pm for $\mathrm{H_3Sn{-}SnH_3}$). Interestingly, secondary intermolecular $(\mathrm{Sn\cdots Cl})_2$ contacts (329 pm) between two neighboring $\mathrm{Sn_2N_2}$ rings were found in the solid-state which explains the low frequency shift of ^{119}Sn in the solid-state (Note, that calculations for the "free" $\mathrm{Sn_2N_2}$ ring yielded a calculated chemical shift of $\delta = 641$ ppm!). Furthermore, quantum chemical calculations predicted the singlet state to be favored by 14 kcal mol^{-1} ($-\Delta E_{\mathrm{S-T}}$). Despite this relatively



Scheme 30. Synthesis of 1,3-diaza-2,4-digermacyclobutanediyl **110** as reported by Power et al.

small singlet–triplet gap (cf. −17.2 kcal mol^{-1} for the Bertrand biradical **93**) Cox and Lappert suggested that the most appropriate description of **108** is a pseudo 6π-electron four-center system. Furthermore, the VB structure **B** shown in Scheme 29 was proposed, which is in close relationship to the one proposed above for the Niecke-type biradicals (cf. Scheme 8).

Almost at the same time, and independently, Power and co-workers [121] published a closely related, bis(imide) bridged germanium compound, $(Ar'Ge)_2(\mu\text{-}NSiMe_3)_2$ (**110**), consisting of large aryl substituents ($Ar' = 2,6\text{-}Dipp_2C_6H_3$, Dipp = 2,6-*i*-$Pr_2C_6H_3$) attached to germanium (Scheme 30).

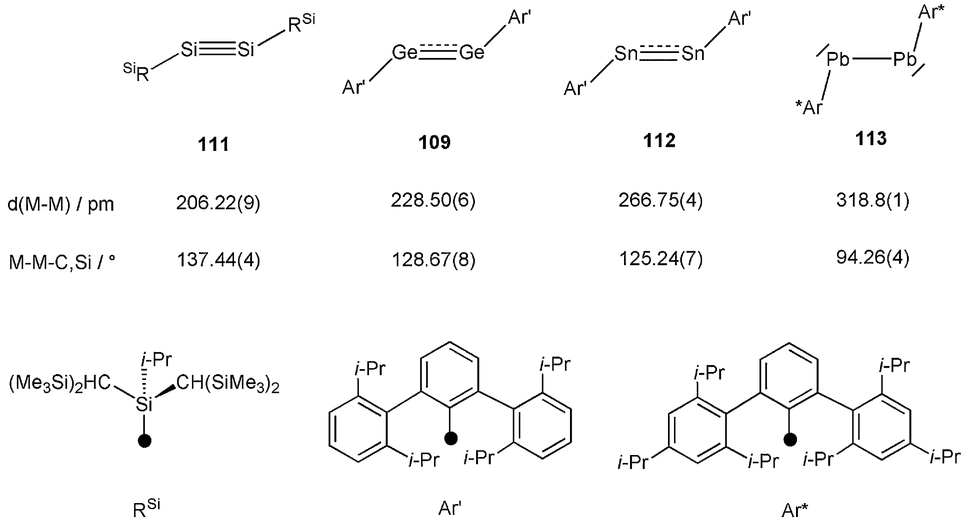
Extremely air and moisture sensitive, dark violet crystals of **110** were isolated in high yield upon treatment of Ar′GeGeAr′ (**109**) with trimethylsilyl azide. In the solid-state, **110** adopts a perfectly planar Ge_2N_2 core featuring trigonal-planar coordinated nitrogen ($\Sigma^\circ = 359.97(8)^\circ$ and pyramidal germanium ($\Sigma^\circ = 322.10(7)^\circ$) constituents with the bulky aryl substituents arranged in a *trans* fashion. The Ge···Ge separation of 275.5 pm is about 30 pm longer than a normal Ge–Ge single bond and comparable to other bridged compounds without germanium–germanium bond. Although the long Ge···Ge separation suggests biradicaloid character, no EPR signal was detected between 77 and 300 K. The calculated HOMO corresponds mainly to a non-bonding combination centered on Ge with weak Ge–C (and minor nitrogen) components. The singlet–triplet separation was calculated to $\Delta E_{S\text{–}T} = -17.5$ kcal mol^{-1} which is comparable to the value found for **93**. The HOMO–LUMO gap of 58.0 kcal mol^{-1} directly corresponds to the energy difference (54.9 kcal mol^{-1}), which was extracted from UV/vis experiments ($\lambda_{max} = 521$ nm) of **110**. Although no LUMO occupation numbers were reported, Power suggested the occupancy of the LUMO to be similar to the Bertrand biradical **93** for which values between 0.17 and 0.19 e$^-$ were calculated (*vide supra*). Compound **110** shows a high reactivity towards solvents as well as facile addition of H_2 to give a product that has been identified tentatively as $Ar'(H)Ge(\mu\text{-}NSiMe_3)_2Ge(H)Ar'$.

6.2. Heavier alkyne analogues REER

It turned out that multiple bonding involving heavier main group elements is considerably more complicated than anticipated. The term alkyne analogue, REER, does not necessarily imply that each of the three valences available for the Group 14 element contribute equally to chemical bonding in order to retain a triple bond featuring an integer bond order of three. Consisting of gradually increasing, non-linear, *trans*-bent geometries as descending the group, a considerable weakening of one component of the degenerate π-bonding was suspected (Scheme 31).

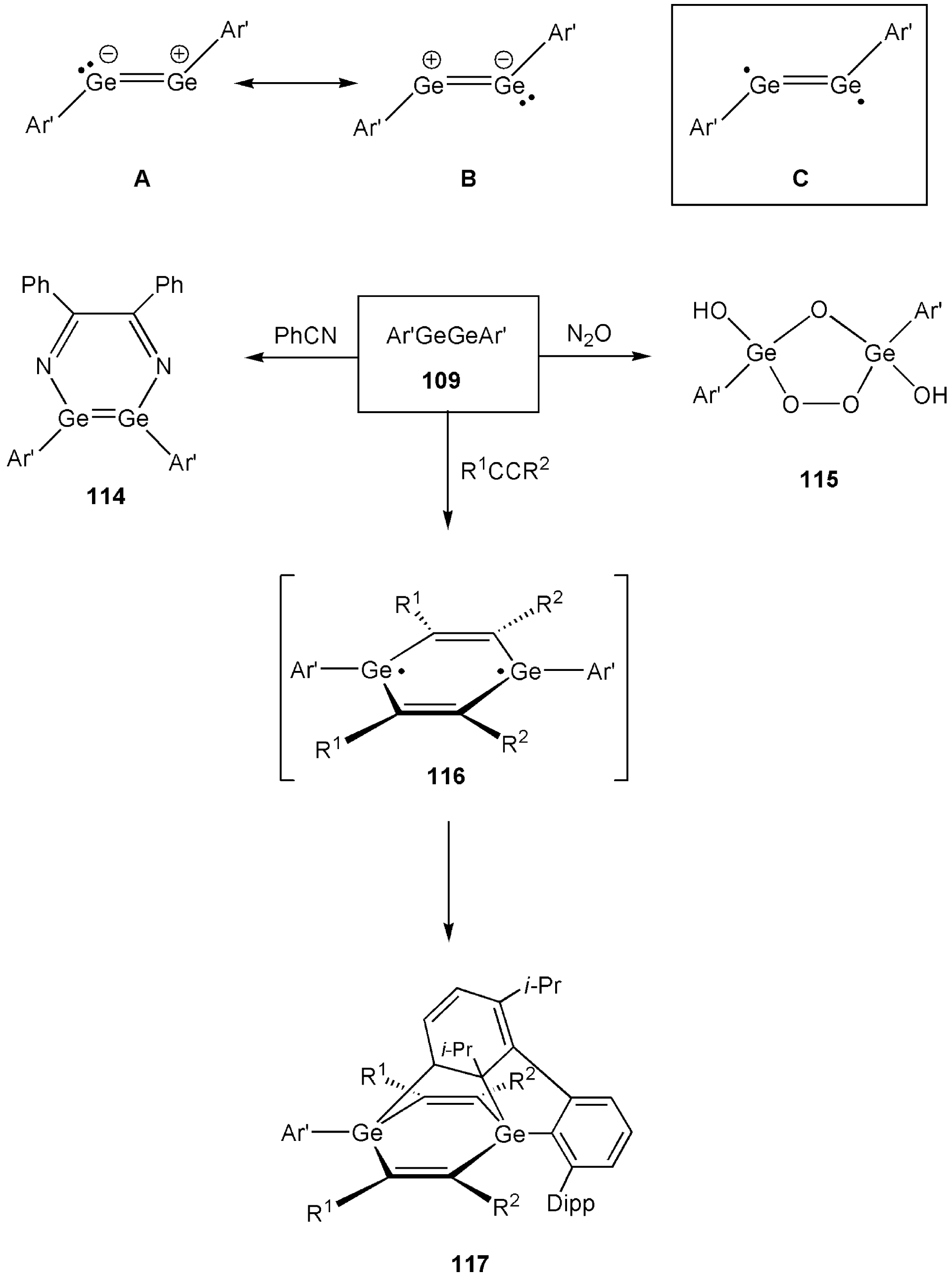
It is believed that the bonding in the germanium species is close to that represented by structures **A** or **B** in Scheme 32 featuring an approximate germanium–germanium double bond and a single lone pair that resonates between positions at each Ge atom. Furthermore, it is possible to represent the structure of **109** as the singlet biradicaloid form **C** and this form is supported by calculations. All given representations of the structure of **109** certainly suggest high reactivity. Indeed, in the course of their ongoing research concerning the chemical reactivity of heavier Group 14 element alkyne analogues, of which the reaction of **109** with trimethylsilyl azide is only one example, Power and co-workers [122] noticed the highly reactive nature of the germanium–germanium multiple bond in **109**. Several investigations including site specific reactivity, cyclovoltammetry, and redox-behavior provide strong support for the notion that the Ge–Ge double bond-resonating lone pair models **A** and **B** make a large contribution to the bonding in **109**. However, the metal–metal bond is homonuclear and is formally non-polar which suggests that the singlet biradical form **C** may be significant. This possibility was already raised by Popelier et al. [123] and is supported by very recent computational data of Power and Head-Gordon [124] where significant biradical character is calculated for the germanium model species MeGeGeMe [125].

Experimental support for the biradical behaviour of **109** stems from several of its reactions, e.g., coupling of PhCN to pro-



	111	109	112	113
d(M-M) / pm	206.22(9)	228.50(6)	266.75(4)	318.8(1)
M-M-C,Si / °	137.44(4)	128.67(8)	125.24(7)	94.26(4)

Scheme 31. Schematic drawings of the alkyne analogues, REER (**109**, **111**–**113**, with E = Group 14 element), comprising bulky silyl and aryl ligands (R^{Si}, Ar′, and Ar*).



Scheme 32. Possible representations (**A**–**C**) of the bonding in Ar′GeGeAr′ (**109**); selected examples of the reactivity of **109**.

duce the NC(Ph)(Ph)CN moiety in **114** or the reaction of **109** with N_2O to produce the peroxo species **115**. Both products provide evidence for reductive coupling reaction, that is an initial one-electron reduction of the substrates (PhCN or N_2O) by a loosely coupled electron at each germanium and subsequent C–C (**114**) or O–O (**115**) bond formation. In contrast, very recent investigations of Tokitoh and co-workers [126] on a closely related digermyne (BbtGeGeBbt) [127] showed no biradical behavior in the reactions with H_2O, Et_3SiH, and 2,3-dimethyl-1,3-butadiene.

The involvement of biradicaloid structures in the germanium derivatives obtained from **109** is also noteworthy, of which the Ge_2N_2 ring compound **110** may serve as one example. Another intriguing intermediate was proposed in the reaction of **109** with alkynes such as $Me_3Si–C≡CH$ or Ph–C≡C–C≡C–Ph which produced the six-membered ring intermediate **116** as shown in Scheme 32 [128]. Formally, this ring has six π-electrons, but instead of being stable and aromatic, it may be considerably biradicaloid. According to its 1,4-biradical character, this intermediate activates a C=C bond in one of the flanking Dipp rings to give **117**.

7. Conclusions

The theory of chemical bonding is still intriguing and of fundamental importance. The search for extremely long or extremely short bonds [129] has yielded many interesting structures and important insights into the nature of chemical bonds. Nevertheless, neither short element–element distances necessarily imply bonding interaction nor long do the opposite, especially when heavier main group elements are involved. This occasionally unforeseeable (but nontheless extraordinary) 'beauty' of main group element compounds has facilitated the isolation and characterization of biradical(oid)s. Without doubt, the biradical character of most of the compounds is far less than most other well-known organic biradicals, although still much more than normal closed-shell molecules. This originates from considerable direct orbital overlap or competing electronic interactions such as transannular through-space interactions between the two radical sites and through-bond neighboring group interactions. The price to pay for gaining stability is certainly the reduction of the biradical character. However, at the current *status quo* of research it is too early to apply general rules for the spin preference or overall reactivity, which is mainly due to very subtle aspects influencing the molecular electronic structure of these type of biradicaloids. Nevertheless, the fascinating features of biradicaloids raise up fundamental questions concerning seemingly simple topics such as the bond-breaking process: *To what extent may a chemical bond be stretched and at which distance should an element–element interaction not be considered as chemical bond any more*? To fully understand the interactions in main group element biradicals is of crucial significance and many elementary questions remain to be answered. Whatever might be the final conclusion about the nature of biradicals, the recent developments in this area undoubtedly inspire scientists from a theoretical and experimental point of view; they will certainly encourage others to put experimental efforts in the research area of biradicals of main group elements—and many permutations are offered by the periodic table of the elements. The combination of both the well-directed syntheses of further biradical(oid) compounds and their precise characterization on one hand, as well as their quantum chemical description on the other, may facilitate an accurate estimation of their intrinsical electronic characteristics. Alongside with such fundamental issues, potential impact on the design of new materials with interesting optical, electronical and spin properties are also conceivable. The main objective for experimental as well as theoretical chemists is undoubtedly to put synergetic efforts in this field. This review article will finish with Power's words: [122b] "*The significance of biradicaloid structures in the reactivity of several classes of main group compounds is just beginning to be recognized*" [130].

Acknowledgements

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[1] Due to numerous papers/books concerning the topic "biradicals", only a selection can be presented here. The reader is referred to the following literature:
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