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Odd-Electron Bonds and Biradicals in Main Group Element Chemistry[**]

Hansjörg Grützmacher[*] and Frank Breher

Radicals play a crucial role in bond-forming and bond-breaking processes.[1] In hydrocarbon chemistry, however, carbon-centred radicals are usually observed as rather short-lived intermediates.[2] Some selected recent examples serve as highlights to demonstrate that in main group element chemistry (apart from C) such reactive intermediates can be stabilized even to such an extent that they can be isolated in crystalline form.

Odd-Electron Bonds

To study the generation of a new type of a genuine two-center, one-electron (2c1e) P–P bond, Geoffroy, Mathey, Le Floch et al.[3] developed the macrocyclic system **1**. Compound **1** contains two phosphinine units, PC_5R_5, which are linked by two flexible siloxane bridges to form a twelve-membered heterocycle. In the ground state conformation, the two phosphinine ring planes are almost coplanar and the two phosphorus atoms approach each other to a distance of 3.26 Å (Scheme 1).

This neutral precursor can be reversibly reduced at a potential of $E^\circ_{1/2} = -1.85$ V and $E^\circ_{1/2} = -2.10$ V (scan rate $5\,V\,s^{-1}$, THF) to give the radical anion **2** and the dianion **3**, respectively. Chemically, **1** was reduced with sodium naphthalenide. The combination of the results from X-ray analyses of the neutral precursor **1** and the fully reduced dianion **3** with the results from EPR spectroscopy and DFT calculations for the persistent phosphorus radical anion **2**, demonstrated that in this case the unpaired electron resides in the single-occupied molecular orbital (SOMO; Scheme 1). This SOMO is partially delocalized over both phosphinine rings, but mainly localized in a P–P σ bond. Notably, the P–P distance in **2** has shortened considerably and lies between that of the neutral compound **1** and that of the fully reduced form **3**, in which a 2c2e P–P bond has formed and the phosphinine rings deviate strongly from planarity.

The formation of the P–P bond in **2** and **3** resembles the creation of S–S bonds in the intensively studied radical cations of type **II** and dications of type **III** of polysulfur compounds (Scheme 1, bottom).[4] The chemical process of bond making and the electronic configuration is different in these sulfur compounds. In the neutral precursor **I**, the nonbonding electron pairs of the two –S– entities interact to

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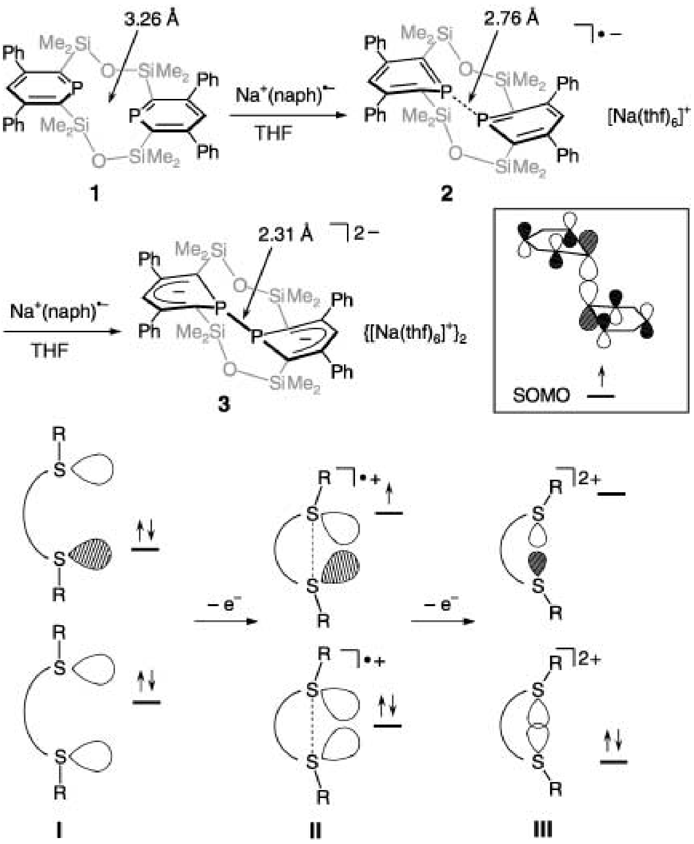
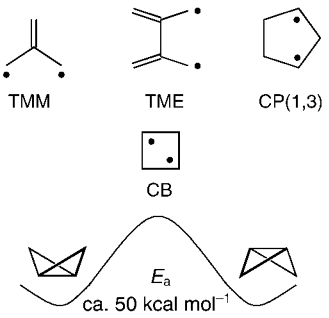


Scheme 1. Generation of a 2c1e P–P bond (top) and 2c3e S–S bond (bottom).

give a bonding and antibonding combination. One-electron oxidation leads to the radical cation $[>S{\cdot}{\cdot}S<]^{\cdot+}$ **II** with a 2c3e bond.[5] Note that although the bond orders in **2** and **II** are the same (b.o. = 0.5), the single electron occupies an S–S antibonding orbital in **II** but a P–P bonding orbital in the radical anion **2**. Often, the radical cations **II** have lower oxidation potentials than their precursors which make their direct observation difficult.

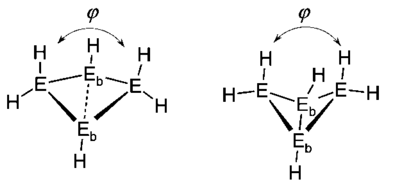
Biradicals (Biradicaloids)

In the above-mentioned radicals, one unpaired electron is delocalized over two main group element centers forming either a 2c1e or 2c3e bond. Even closer to bond-forming and bond-breaking processes are biradicals,[6] which in many cases are more appropriately designated as biradicaloids.[7] These may be roughly divided into two classes: 1) delocalized biradicals (non-Kekulé molecules)[8] for which trimethylenemethane (TMM)[9a] and tetramethyleneethane (TME)[9b] are the archetypal examples; 2) localized biradicals with two well-defined radical substructures that are not conjugated by way of a classical π system. Typical examples of this class are cyclopentane-1,3-diyl (CP(1,3))[10] or cyclobutanediyl (CB).[11] In all of these radicals the single electrons reside in π-type orbitals and the individual spins may either couple to give a triplet (TMM, TME) or a singlet state (CP(1,3)). The triplet states of CBs could be observed because the barrier for spin conversion impedes the ring closure to the corresponding bicyclo[1.1.0]butanes. On the other hand, singlet cyclobutanediyls are only predicted as transition states for the ring inversion of [1.1.0]cyclobutanes at about 50 kcal mol^{-1} (Scheme 2).[12]



Scheme 2. Formulas of the delocalized biradicals trimethylenemethane (TMM), tetramethyleneethane (TME) (non-Kekulé molecules) and localized cylopentane-1,3-diyl (CP(1,3)) and cyclobutanediyl (CB).

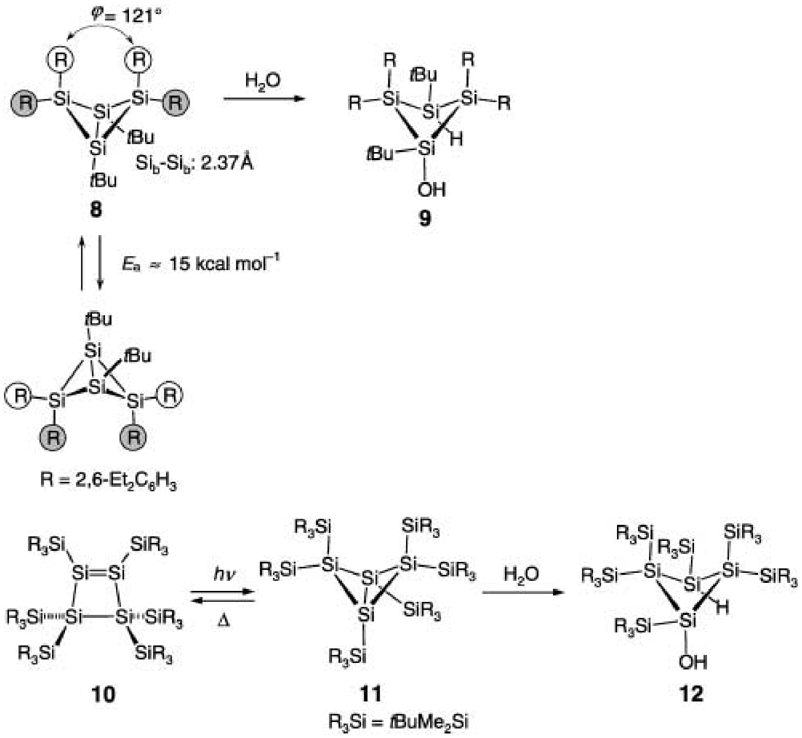
Strained Group 14 element compounds were identified as suitable candidates for the synthesis of stable biradicaloids (Scheme 3).[13] For the silicon, germanium, tin, and lead analogues of bicyclo[1.1.0]butanes, quantum-chemical calculations[13b, 14a–c] predict the phenomenon of bond stretch isomerism,[15] that is two distinct minima on the potential energy surface (PES) which mainly differ by the length of one bond, as a result of the high ring strain and intrinsically low σ-bond energies. For the silicon and germanium compounds, the bond stretch isomers **4** and **5**, which can be regarded as coupled π-type biradicaloids, are more stable by about 8 and 16 kcal mol^{-1}, respectively, than the isomers **4′** and **5′** which possess usual E–E bond lengths. For E = Sn, Pb only the isomers **6** and **7** with an elongated E_b–E_b bond between the bridgehead atoms are found as minima.



		E_b-E_b[Å]	φ[°]		E_b-E_b[Å]	φ[°]
4	E = Si	2.78	142	**4′**	2.37	123
5	E = Ge	3.03	144	**5′**	2.48	118
6	E = Sn	3.71	144			
7	E = Pb	3.90	152			

Scheme 3. Calculated bridgehead E_b–E_b bond lengths [Å] and interplane angles φ [°] for tetrametallabicyclo[1.1.0]butanes of Group 14.

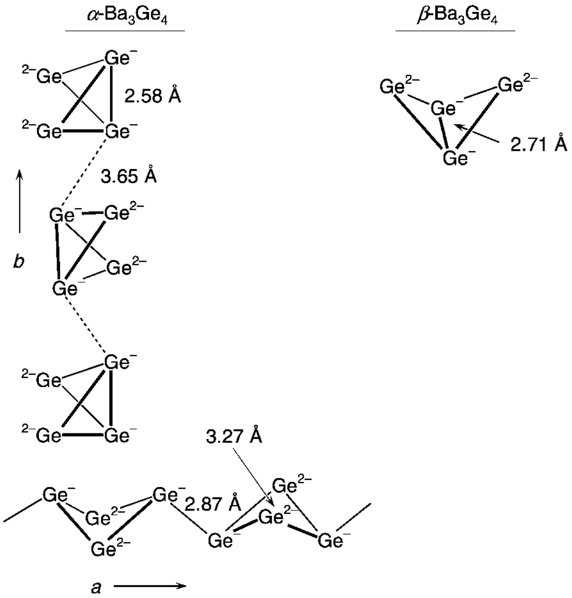
Synthetically accessible and structurally characterized tetrasilabicyclo[1.1.0]butanes are rare. The sterically encumbered derivative **8** has a normal Si–Si bond length of 2.37 Å (Scheme 4).[16] This is in accord with computations which predict that σ-electron-donating groups, for example *t*Bu, at the bridgehead silicon atoms favor the closed form, while σ-electron-withdrawing substituents, for example F, at the bridging silicon atoms favor the open form.[13b, 14a] However, the physical and chemical properties of **8** indicate the energetically close relationship to the biradicaloid form.



Scheme 4. Experimentally studied tetrasilabicyclo[1.1.0]butanes **8** and **11**. The inequivalent R groups that are interconverted by ring inversion are indicated by white and gray circles.

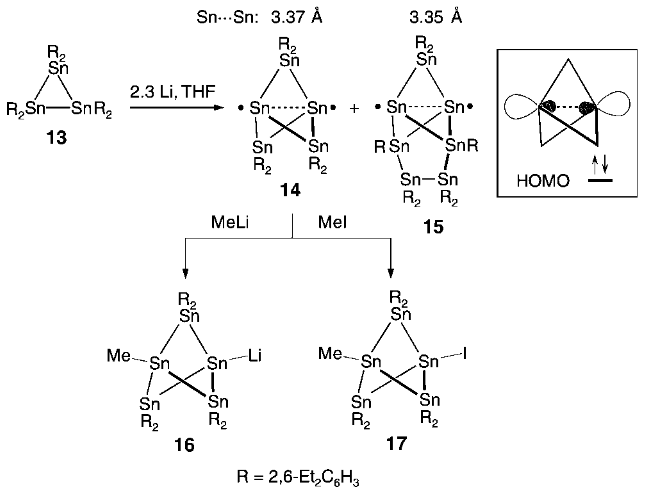
Crystals of **8** are thermochromic (intensely yellow at 170 °C, colorless at −196 °C) and the ring-inversion barrier for **8** is low ($E_a \approx 15\,\mathrm{kcal\,mol^{-1}}$), as estimated by NMR methods from the coalescence of the inequivalent R groups. Also, the central Si_b–Si_b bond is unusually reactive; even water can be quantitatively added to give the hydroxy derivative **9**. A similar observation was made for the silyl-substituted tetrasila[1.1.0]bicyclobutane derivative **11**, which was generated from the tetrasilacyclobutene derivative **10** under irradiation with light ($\lambda > 420$ nm).[17] In the photostationary state, 91 % conversion was reached, and **11** was quenched by hydrolysis at 0 °C to give **12**. No further spectroscopic data were obtained for **11** because in the dark it rearranges quantitatively to the cyclobutene **10** (Scheme 4). Remarkably, this isomerization cycle can be repeated more than 10 times without notable side reactions. In contrast to these results, computations for the parent system predict that the bicyclobutane isomer should be thermodynamically more stable.[14d] On the other hand, such rearrangements, biradicaloid $\rightleftharpoons$ cyclobutenoid, have some common character and predictions concerning the relative stabilities of the individual isomers may be highly substituent dependent (for another example see **20** $\rightleftharpoons$ **23** in Scheme 7).

To our knowledge no other stable molecular metallabicyclobutanes of the heavier Group 14 elements have been reported to date; however, an interesting example of bond stretch isomerism and indications for biradicaloids in solid-state chemistry has been reported for the Zintl phase Ba_3Ge_4. This system is prepared from a stoichiometric reaction of the elements between 1120 and 1360 K.[18] In the high-temperature β-modification only isolated $[Ge_4]^{6-}$ ions with the butterfly bicyclo[1.1.0]butane structure are formed. The bridgehead Ge_b–Ge_b bond is long (2.71 Å), although shorter than the computationally predicted bond length of 3.03 Å. In the room-temperature stable α-modification, one half of the $[Ge_4]^{6-}$ units exist as isolated ions with short Ge_b–Ge_b bonds (2.58 Å) that are aligned along the crystallographic *b* axis (*inter*molecular Ge–Ge contacts: 3.65 Å). The other half forms a polymeric $[Ge_4]^{6-}_{\infty}$ chain along the *a* axis. In this polymeric anion, the *inter*molecular Ge–Ge bonds of 2.87 Å replace the *intra*molecular Ge_b–Ge_b bonds which are elongated to 3.27 Å. As indicated in Scheme 5, neither the number of Ge–Ge bonds nor the charges change during the polymerization process nor the bivalent and trivalent germanium atoms are interchanged. Quantum-chemical considerations show that the intermolecular Ge_b–Ge_b bonds in the polymeric anion have considerable biradicaloid character. Surprisingly, although all calculations indicate a diamagnetic ground state a sizable temperature-dependent paramagnetism was observed which leaves the question open whether this is due to accessible triplet states or to impurities in the sample.



Scheme 5. Section of the anionic substructure of the α- and β-modification of Ba_3Ge_4. The long intermolecular contacts between the isolated $[Ge_4]^{6-}$ ions represented by dotted lines. In the polymeric anion $[Ge_4]^{6-}_{\infty}$ these distances are shortened and replace the elongated bridgehead Ge_b–Ge_b bonds.

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. This was impressively demonstrated by Sita and Kinoshita who succeeded in isolating the pentastanna[1.1.1]propellane **14** (31 % yield) and the derivative **15** (1 % yield) from the reduction of the cyclotristannane **13** with lithium in THF (Scheme 6).[19]



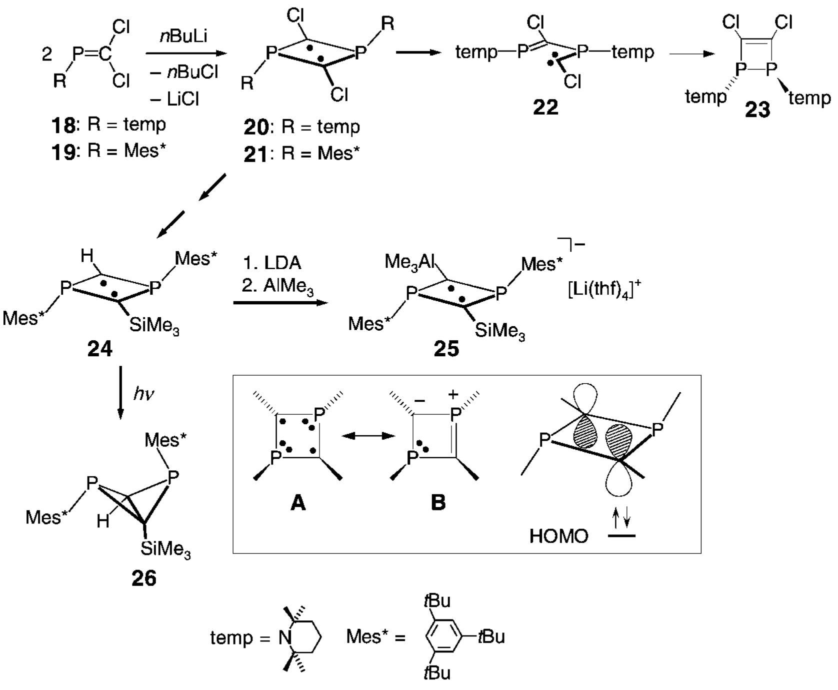
Scheme 6. Synthesis and reactivity of pentastanna[1.1.1]propellanes.

The experimentally determined distances (X-ray analyses) between the bridgehead tin atoms Sn_b are 20% longer than a regular Sn–Sn single bond. That **14** and **15** have considerable singlet biradicaloid character is further corroborated by the ease by which both compounds can be reduced stepwise to give the radical anions $\mathbf{14}^{\bullet -}$ and $\mathbf{15}^{\bullet -}$ ($E^{\circ}_{1/2} \approx -1.4$ V versus NHE) and the dianions $\mathbf{14}^{2-}$ and $\mathbf{15}^{2-}$ ($E^{\circ}_{1/2} \approx -1.9$ V versus NHE), respectively. The formally electron-deficient bridgehead tin centers (seven valence electrons) are converted into eight-valence-electron-configured $(SnR_2)_3Sn^-$ entities. Also, **14** showed some unusual reactivity; for example, MeLi or MeI are cleanly added to the central Sn_b–Sn_b bond to give **16** and **17**, respectively (Scheme 6). Extensive ab initio calculations performed for E_5[1.1.1]propellanes (E = C, Si, Ge, Sn),[20] support the idea that although a bond-critical point indicative of a classical covalent bond can be found only for the carbon compound, there is a strong through-space interaction between the bridgehead centers in the σ-type biradicaloids for E = Si–Sn.

The first biradicaloid species prepared in gram quantities (yields >60%) were the 1,3-diphosphacyclobutane-2,4-diyls **20** and **21**. These were isolated when two equivalents of the *C*-dichlorophosphaalkenes **18** or **19**, respectively, were allowed to react with one equivalent of *n*BuLi at −100 °C (Scheme 7).[21] The ring skeleton of these highly unusual P_2C_2 heterocycles is planar but both the carbon and the phosphorus centers are embedded in pyramidal coordination spheres. The comparatively high inversion barriers at phosphorus impede the formation of a planar 6π-conjugated heterocycle (like in the isoelectronic S_2N_2)[22] and **20** and **21** have a high biradicaloid character. On the other hand, the coordination sphere at the phosphorus 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.

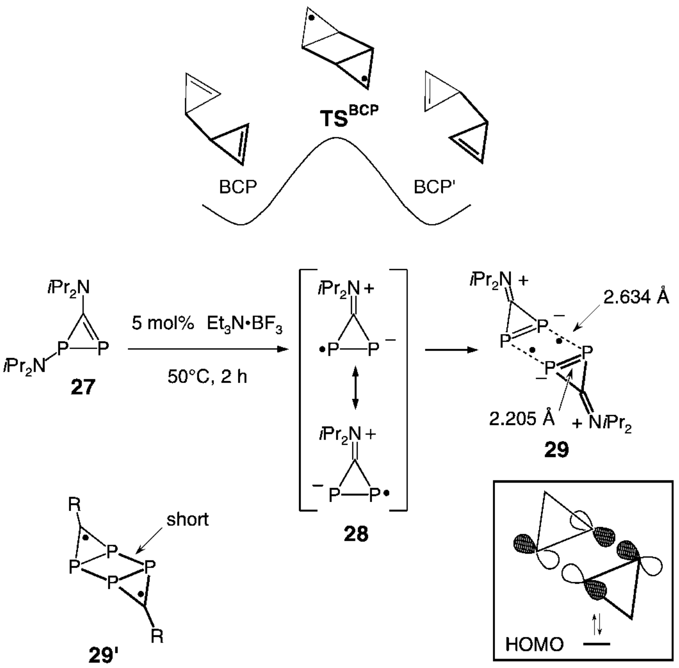
Simplistically, the electronic ground state may be approximated by the resonance structures **A** and **B** shown in Scheme 7 and diphosphacyclobutane-2,4-diyls may be described as weakly π-conjugated (delocalized) biradicaloids. Recent calculations by Schoeller et al. show that especially the substituents at the radicaloid carbon centers influence the electronic configuration of these Niecke biradicals; for example, C-bonded silyl groups (σ donor, π acceptor) stabilize the singlet state, while the combination, NR_2 group at phosphorus and alkyl group at carbon, lowers the energy of the triplet state, thus providing the opportunity to easily control the biradical spin state.[21e]

The pioneering preparative work to these biradicaloids was performed by Niecke et al. While the P-amino derivative **20** is unstable at room temperature and isomerizes rapidly and quantitatively in solution, and slowly even in the solid state, to the 1,2-dihydrodiphosphete **23**, the Mes*-substituted compound **21** is stable up to 150 °C. The chloro substituents in **21** can be exchanged for a silyl group and a H atom to give **24**. This compound can then be deprotonated by lithium di(isopropyl)amide (LDA) to give an unusual anionic carbene which subsequently reacts with $AlMe_3$ to give the anionic Niecke biradical **25**. The symmetry of the HOMO shown in Scheme 7 does not allow a thermal ring closure of the open P_2C_2 heterocycles to the thermodynamically more stable valence isomer 2,4-diphosphabicyclo[1.1.0]butane; however, photolysis leads almost quantitatively to **26**.

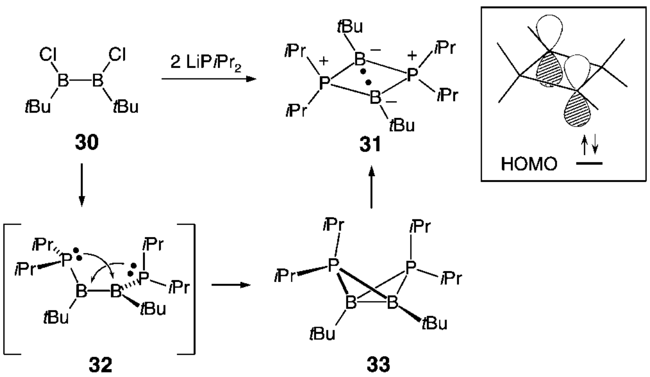


Scheme 7. Syntheses of 1,3-diphosphacyclobutan-2,4-diyls (Niecke biradicals).

Biradical structures are also found among the more than 200 possible valence isomers of the formula C_6H_6. For the Cope rearrangement of the bicycloprop-2-enyl BCP one such structure is proposed as a transition state $\mathbf{TS}^{\mathrm{BCP}}$ (Scheme 8).[23] Replacement of the four carbon atoms in the central four-



Scheme 8. Cope rearrangement of bicycloprop-2-enyl BCP⇌BCP′ and synthesis of the stable diphosphirenyl dimer **29**.



Scheme 9. Synthesis of the Bertrand biradical **31**.

membered ring by phosphorus atoms leads to compounds of type **29** which are no longer transition states but are stable.[24] Bertrand et al. synthesized **29** from the reaction of the 1*H*-diphosphirene **27** with a catalytic amount of $NEt_3 \cdot BF_3$, and isolated it in the form of red crystals in 45% yield. It seems likely that the diphosphirenyl radical **28** is generated as the intermediate in this reaction. According to calculations by Schoeller the unpaired electron in **28** is equally distributed over both phosphorus atoms and localized in the π^* orbital of the P=P bond. It is hence understandable that dimerization of **28** occurs through a $\pi^*-\pi^*$ interaction[25] and leads to the observed product **29**. The central P_4 framework can be best described as a 4c6π-electron system in which four π electrons are hosted in two P=P bonds within each CP_2 ring and the remaining two π electrons are localized in the HOMO (Scheme 8). Thus formally the two CP_2 units are held together by two one-electron P–P bonds, as indicated by the formula given in Scheme 8. This description is consistent with the observation that the intra-ring P–P bonds are quite short, while the inter-ring P–P bonds are very long (c.f. **2** in Scheme 1). A further inspection of the electronic properties of compounds of type **29** by quantum-mechanical calculations[24, 26] predict that they can be transformed into genuine biradicals like **29′** by compression of the central P_4 ring along the long P–P vectors. This could be achieved either by changing the amino groups at the ring carbon atoms for alkyl or especially aryl groups, whereby the unpaired electrons will localize at the C-carbon atoms.[26] It may also be possible to achieve this transition by applying pressure on the system.[26] These exciting possibilities await, however, experimental verification.

As the icing on the cake, Bertrand, Schoeller et al. have recently successfully synthesized the crystalline, localized singlet, boron-centered biradicaloid **31** (Scheme 9).[27] The $(RP)_2(CR)_2$ motif of the Niecke radicals was replaced by the isoelectronic $(R_2P)_2(BR)_2$ unit (both contain 22 valence electrons for R = H). This had two important consequences for the stability: 1) the contribution of resonance structure **B** (Scheme 7) to the electronic ground state is largely diminished because the phosphorus lone pair has been transformed into a P–C σ bond; 2) the heterocycle in **31** is expanded because of the intrinsically longer P–B bonds (1.89 Å; the P–C bonds in **20**, **24**, and **25** are 1.73–1.76 Å). Both factors favor an open singlet-biradical form.

The synthesis of **31** proved to be simple: reaction of the 1,2-dichlorodiborane(4) **30** with two equivalents of the secondary lithium phosphide $LiP(iPr)_2$ furnished **31** as yellow, air-sensitive but thermally highly stable (>200 °C) crystals in 63% yield. The X-ray structure analysis revealed a perfectly planar P_2B_2 ring in which the transannular B–B distance (2.57 Å) is 38% longer than the longest B–B bond reported so far.[28] Interestingly, ab initio calculations show that for the parent molecule $(H_2P)_2(BH)_2$ the planar form would be the transition state at 16.4 kcal mol^{-1} for the inversion of the 1,3-diphospha-2,4-diborabicyclo[1.1.0]butane **33**. Note also that the symmetry of the HOMO shown in Scheme 9 allows a thermal disrotatorial electrocyclic ring closure. Although the mechanism is not known in detail, it can be assumed that the 1,2-diphosphanyldiborane(4) **32** should be one of the initial reaction intermediates. This structure, likely in a staggered conformation, should rapidly rearrange into the 1,3-diphospha-2,4-diborabicyclo[1.1.0]butane **33** which contains enough potential energy from the bulky groups to spring apart to give **31**. In other words, the choice of the sterically demanding substituents that can be comfortably accommodated in the planar form of **31** allowed the crystallization of a strictly iso(valence)electronic and *isostructural* transition state analogue for the bicyclo[1.1.0]cyclobutane, C_4H_6, inversion. Using other substituents, it should be possible to adjust the B–B distance such that any conformation on the internal reaction coordinate (IRC) for the bicyclo[1.1.0]butane inversion can be investigated. Futhermore, such studies on the transition of biradicaloids to biradicals (where 100% unpaired spin density would be confined to one radical site) would allow fundamental deep insights into the coupling of electronic spins.

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Conclusion

Clearly, biradical(oid)s with main group elements are intrinsically more stable than their hydrocarbon counterparts. And many combinations are offered by the periodic system! Furthermore, the properties of biradicaloids can be fine-tuned by varing the substituents. Generally, the potential energy surfaces containing isomers of main group element compounds are much flatter than for comparable hydrocarbons. This facilitates the control over their distribution and mutual interconversions within a reasonable temperature range. From a purely synthetic point of view, the introduction of sterically demanding but electronically very different substituents is often easier to achieve in main group element chemistry than in classical hydrocarbon chemistry (simple salt metathesis reactions were involved in most of the above-cited examples, $\mathrm{E{-}Hal} + \mathrm{R^-} \rightarrow \mathrm{E{-}R} + \mathrm{Hal^-}$). Quantum-chemical calculations proved to be a highly valuable tool to guide the synthetic efforts for bi- and polyradicals, for the design of the electronic configuration, and finally for the development of new materials. As Berson wrote:[6c] "In this domain of chemistry one has to expect the unexpected and to be ready to find it." Hopefully, this highlight will stimulate further interest and research efforts in this direction.

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