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Vol. 80 Commemorative Accounts

Let's Play with Valence Isomers: The Influence of Different Main Group Elements on Their Relative Stability

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Valence isomers are compounds featuring the same fragments connected in different ways. In this personal account, we describe how we first met by serendipity this kind of isomerism, and how later on we used the specific properties of phosphorus and boron to prepare two types of valence isomers that are not accessible with elements exclusively from the first long row. In the carbon series, benzene is calculated to be 608 kJ mol^{-1} lower in energy than its singlet diradical valence isomer, the *anti*-tricyclohexylene, but a tetraphosphorus analogue of the latter has been isolated. According to calculations, the parent amidinium salt is 541 kJ mol^{-1} more stable than its three-membered heterocyclic valence isomer, but in the phosphorus series, the difference in energy between the open and closed forms is only a few kJ mol^{-1}; provided the right substituents are used, the cyclic form can be isolated. Lastly, among butadiene valence isomers, singlet cyclobutane-1,3-diyls were predicted only as transition states for the inversion of bicyclo[1.1.0]butane. In marked contrast, 1,3-dibora-2,4-diphosphacyclobutane-1,3-diyls can be prepared by valence isomerization of the corresponding butadiene derivatives and isolated under conventional experimental conditions.

Isomers are compounds that have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Applying this definition to C_6H_6 would lead to more than 330 isomers featuring tetravalent arrangement around all carbons.[1] Even, excluding the diastereomers and enantiomers, a computer-aided procedure generated 217 possible C_6H_6 isomers.[2] In 1966, in order to better classify all these isomers, Romanian chemist Balaban defined an interesting new type of isomeric relationship that he named "valence isomerism."[3] Valence isomers of benzene were described by the formula $(CH)_6$, each carbon bearing a single hydrogen. In other words, valence isomers of benzene differ only by the ways in which carbon–carbon single and/or double bonds connect six CH units. This concept of valence isomers can of course be expanded to a variety of compounds using a more general definition, which could be: compounds featuring the same fragments connected in different ways.

In this personal account, we describe how we first met by serendipity this kind of isomerism, and how later on we used the specific properties of phosphorus and boron to prepare valence isomers that are not accessible with carbon and nitrogen.

Indeed, the columns of the Periodic Table help chemists systematize their thinking about reactivity of groups of elements based on their valence. This approach is useful as long as one is aware of the "second row anomaly." The second row elements tend to form hybrids from s and p orbitals that lead to the familiar digonal, trigonal, and tetragonal bonding geometries of carbon. Third row elements largely avoid hybridization. A consequence of this is that third and higher row elements are reluctant to form multiple bonds and to adopt planar geometries. This tendency can be seen in their respective elemental forms (N_2 contains a triple bond, whereas phosphorus forms P–P single bonds in the tetrahedral P_4 molecule), and in their inversion barriers (NH_3: 24 kJ mol^{-1}; PH_3: 156 kJ mol^{-1}). In addition, electronegativity often plays a crucial role.

This account is divided into three parts. First, we report how we discovered by serendipity a tetraphosphabenzene valence isomer, which was the first compound with phosphorus–phosphorus one-electron bonds. Then, we discuss the preparation and structure of diphosphino carbocations, and the discovery of a cyclic valence isomer of a diphosphino analog of an amidinium salt. Lastly, the preparation of stable singlet diradicals by valence isomerization of boron/phosphorus analogs of butadienes is presented (Fig. 1).

A Tetraphosphabenzene Valence Isomer: Less than Two-Electron Phosphorus–Phosphorus Bonds

In contrast to the large number of possible isomers of benzene **I** which are known, so far only four valence isomers have been prepared (Fig. 2).[4] They are the *cis*-Dewar benzene **II** by van Tamelen and Pappas in 1963,[5] the benzvalene **III** by Wilzbach et al. in 1967,[6] the prismane **IV** by Katz and Acton in 1973,[7] and the bicycloprop-2-enyl **V** by Billups and Haley in 1989.[8,9] In addition, to the isolated valence isomers of ben-

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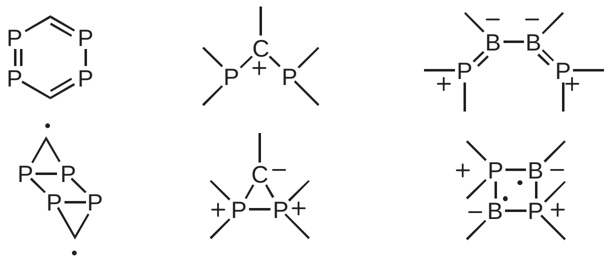


Fig. 1. Tetraphosphabenzene, phosphorus analogs of amidinium salts and phosphorus/boron analogs of butadienes (top), and their respective valence isomers (bottom).

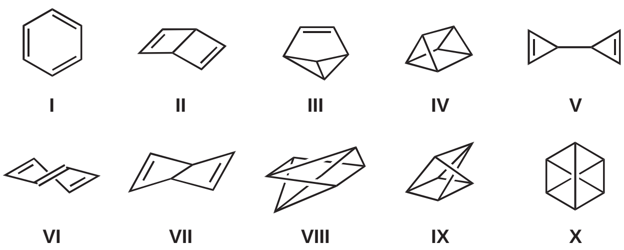


Fig. 2. Benzene **I**, its known **II**–**V**, calculated **VI** and **VII**, and imagined **VIII**–**X** valence-isomers, which respect the rules of classical organic chemistry.

zene, it should be noted that ab initio calculations have predicted that *trans*-Dewar benzene **VI** and “Möbius” benzene **VII** lie in very shallow minima on the potential energy profile, with energies of 660 and $418\,\mathrm{kJ\,mol^{-1}}$, respectively, higher than benzene;[10] therefore they are unlikely candidates to be isolated. It would also be fair to mention three other valence isomers, which have been imagined along the years: the benzmöbiusstripane **VIII** in 1966,[3] the twisted prismane **IX** in 1975,[11] and **X**, which is the structure proposed for benzene by Claus in the 19th century![12]

Compounds **I**–**X** obey the rules of classical organic chemistry, since all carbons and hydrogens are tetravalent and monovalent, respectively. However, one can also imagine a number of valence isomers of benzene with biradical structures. So far, none of these species have been isolated, although *anti*-tricyclohexylene **XI** (Fig. 3) has been postulated[13] to be the transition state in the Cope rearrangement of bicycloprop-2-enyl derivatives of type **V**.

A phosphorus atom is isolobal to a CH fragment, and therefore tetraphosphabenzene $\mathbf{I_P}$ is isolobal to benzene. Similarly, compound $\mathbf{XI_P}$ is isolobal to **XI** and thus is a valence isomer of the tetraphosphabenzene $\mathbf{I_P}$. In 1998, we isolated by absolute serendipity, a derivative of $\mathbf{XI_P}$, and found that it to be the first compound featuring phosphorus–phosphorus one-electron bonds.[14]

At that time, we were working on the preparation of a variety of diphosphorus-containing three-membered heterocycles.[15] We were especially interested in the synthesis and isolation of hitherto unknown diphosphirenyl cations such as **2** (Scheme 1).[16] It was well established that treatment of a phosphine bearing an amino group with trifluoromethane sulfonic acid led to the corresponding phosphenium cation, by heterolytic cleavage of the P–N bond.[17] Having in hand 1*H*-diphosphirene **1**,[15f] we first added a stoichiometric amount of triflic acid, and obtained a very complex mixture of products. We then turned our attention to Lewis acids and chose BF_3. When we used a stoichiometric amount, we obtained again a multitude of products. However, repeating the experiment, but using a tetrahydrofuran solution of $BF_3 \cdot Et_3N$ complex, and only 0.05 equivalent (by mistake), we obtained a very clean reaction. After evaporation of the solvent and extraction with pentane, new compound $\mathbf{11_P}$ was isolated in 45% yield as red crystals (melting point: 140 °C).

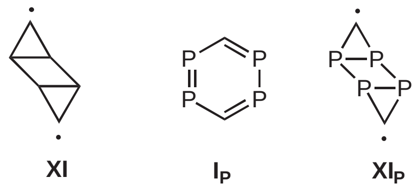
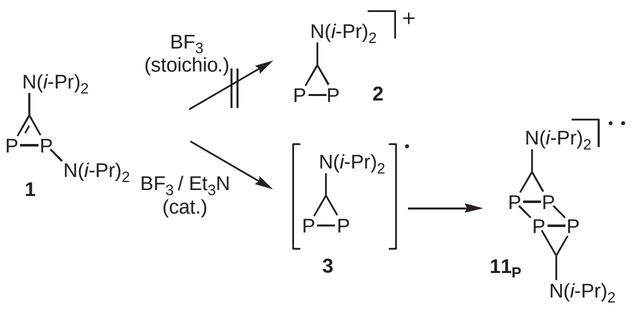


Fig. 3. Anti-tricyclohexylene **XI**, tetraphosphabenzene $\mathbf{I_P}$, and its valence isomer $\mathbf{XI_P}$.



Scheme 1.

The proton-coupled ^{31}P NMR spectrum showed only a singlet at -164.5 ppm, suggesting the presence of a three-membered ring framework,[18] and the absence of amino group directly bound to phosphorus. The ^1H and ^{13}C NMR spectra showed only one *iso*-propyl environment, in addition to a quaternary carbon, which appeared as a pseudo-triplet at low field [162.2 ppm, $J_{PC} = 83$ Hz). These NMR data were those expected for the desired diphosphirenyl cation **2**. However, we were surprised by the high solubility of the compound in pentane, and we quickly found out by ^{11}B NMR that no boron species were present, ruling out the formation of a salt. We carried out a single-crystal X-ray diffraction study. Much to our surprise, the preliminary X-ray data showed a monomeric three-membered ring, resembling the diphosphirenyl radical **3**. Of course these data did not fit with the diamagnetic nature of the compound as shown by NMR. The first clear indication of the real structure of $\mathbf{11_P}$ came from its molecular weight determined by mass spectrometry, and which corresponded to a dimer of the diphosphirenyl radical **3**. Returning to the X-ray analysis, we indeed found the dimeric structure $\mathbf{11_P}$ (Fig. 4) and rapidly understood why the preliminary data showed only half of the molecule: the PP bonds between the two three-membered rings [2.634 Å] were significantly outside the usual range for PP bonds!

To gain a better understanding of the nature of $\mathbf{11_P}$, and especially to explain the existence of the very long PP bonds, ab initio calculations were performed on the model compounds

3a and **11**$_{\mathbf{Pa}}$ featuring NH_2 groups instead of N*i*-Pr_2 substituents. It was found that for **3a** the spin density is equally distributed over the two phosphorus atoms and the SOMO is the π^* orbital of the P=P double bond. In other words, radical **3a** is best described by the zwitterionic structure shown in Fig. 5. The dimerization of the diphosphirenyl radical **3a** then occurs via a π^*–π^* interaction, giving rise to the formation of **11**$_{\mathbf{Pa}}$. A six-π-electron, four-center bonding system best describes the P_4 framework, each phosphorus–phosphorus bond between the two three-membered rings being formally a one-electron bond, which rationalizes the very long PP bond distance.

Before our work, π^*–π^* interactions had already been found in numerous inorganic molecules,[19] including in the solid-state structure of NO,[19a,b] but **11**$_{\mathbf{P}}$ was the first example involving phosphorus atoms, and phosphorus–phosphorus one-electron bonds. Since that time, only two other derivatives featuring phosphorus–phosphorus odd-electron bonds have been isolated (Fig. 6), but importantly they feature different types of bonding situation. The one-electron PP bond in the anion radical[20] obtained by reduction of the corresponding diphosphine, involves the σ overlap of phosphorus p-orbitals (Fig. 6, top). On the other hand, the tricyclic compound (Fig. 6, bottom)[21] results from a SOMO–SOMO (π_3–π_3) interaction between two cyclo-1σ^4,3σ^2,4σ^2-triphosphapentadienyl radicals, and therefore features less-than-one-electron bonds.

Up until the 1970s, the chemistry of the heavier main group elements was believed to be restricted to that involving single bonds as a result of the so-called "double bond rule." During the last three decades a lot of knowledge has been accumulated on four-electron and six-electron multiple bonds.[22] Now, the isolation of the tetraphosphabenzene valence isomer **11**$_{\mathbf{P}}$ and of derivatives in Fig. 6, suggests that one-electron bonds could also play an important role in phosphorus chemistry.[23,24]

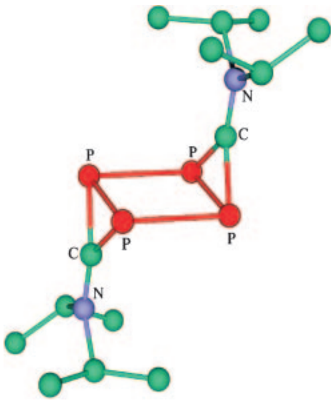


Fig. 4. Molecular view of diradical **11**$_{\mathbf{P}}$ in the solid state.

A Cyclic Valence Isomer of Diphosphorus Analogs of Amidinium Salts

After the serendipitous discovery of the tetraphosphabenzene valence isomer **11**$_{\mathbf{P}}$, we decided to investigate the possibility of using heavier main group elements for preparing unknown valence isomers of well-known types of organic compounds. Our first success was the preparation of a diphosphorus analogue of a cyclic valence isomer of an amidinium salt.[25]

Nitrogen-substituted carbocations, namely the iminium **XII**$_{\mathbf{N}}$ and amidinium salts **XIII**$_{\mathbf{N}}$ are well-known stable species, which have found widespread use in synthetic chemistry, biological processes and molecular material science. Contrastingly, for the heavier analogues, only a few mono-phosphorus-substituted cations, the highly reactive methylenephosphonium ions **XII**$_{\mathbf{P}}$, have been isolated.[26] No experimental studies had been undertaken before our work concerning the diphosphino carbenium ions **XIII**$_{\mathbf{P}}$ (Fig. 7).

The origin of the stability of the amino carbocations **XII**$_{\mathbf{N}}$ lies in the π-donation of the nitrogen lone pair into the formally unfilled 2p(π)-orbital of the adjacent carbon center; this surpasses the σ-attracting effect due to the electronegativity of nitrogen. Although phosphorus is more electropositive than carbon, and of course nitrogen, phosphino carbocations **XII**$_{\mathbf{P}}$ are much less stable than iminium salts **XII**$_{\mathbf{N}}$. This is due to the inferior ability of phosphorus to achieve the optimum planar configuration with sp^2 hybridization, which is a requirement for acting as a π donor. Indeed, as mentioned in the introduction of this account, the inversion barrier at P is much higher than at N (PH_3: 156 kJ mol^{-1}; NH_3: 24 kJ mol^{-1}). Importantly for our purpose, iminium salts **XII**$_{\mathbf{N}}$ react with nucleophiles at

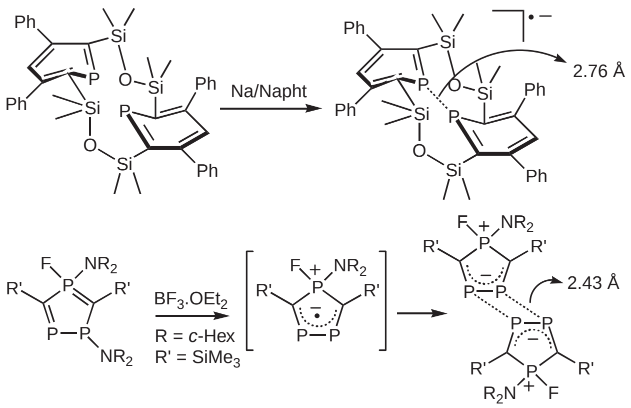


Fig. 6. Two examples of preparation of compounds featuring odd-electron phosphorus bonds, with the corresponding PP bond lengths.

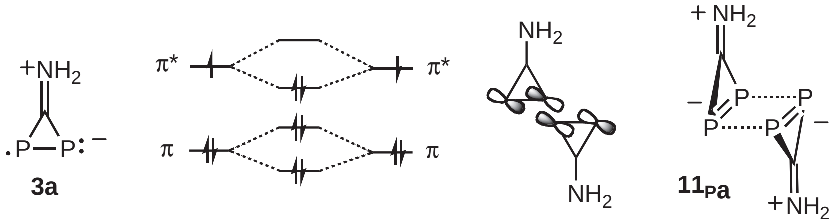


Fig. 5. Canonical structure for **3a**, dimerization via a π^*–π^* interaction, and canonical structure for **11**$_{\mathbf{Pa}}$.

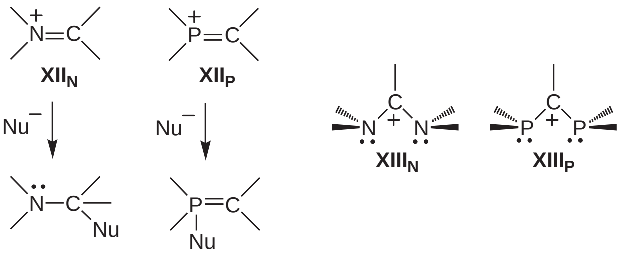


Fig. 7. Iminium $\mathbf{XII_N}$, methylenephosphonium $\mathbf{XII_P}$, and their reactivity towards nucleophiles; amidinium $\mathbf{XIII_N}$, and their diphosphorus analog $\mathbf{XIII_P}$.

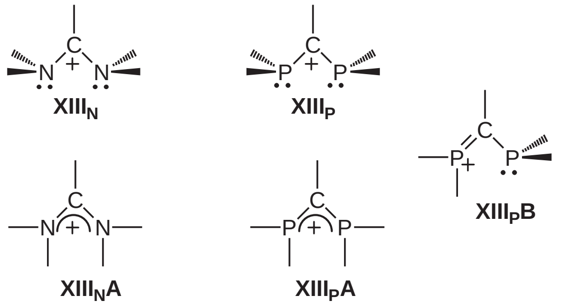


Fig. 8. Schematic structures of amidinium $\mathbf{XIII_N}$, and of their phosphorus analog $\mathbf{XIII_P}$.

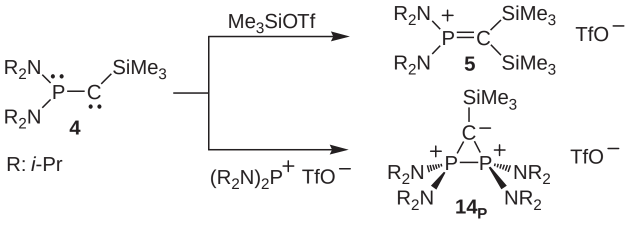
Fig. 9. Rearrangement of diphosphino carbocations $\mathbf{XIII_P}$ into its cyclic carbanionic valence isomer $\mathbf{XIV_P}$.

carbon, whereas methylenephosphonium ions $\mathbf{XII_P}$ react at phosphorus affording the corresponding ylides (Fig. 7).

On the basis of calculated energies of isodesmic reactions using the parent compounds $\mathbf{XII_N}$ and $\mathbf{XII_P}$ (H substituents), introduction of the second amino group stabilizes amidinium ions $\mathbf{XIII_N}$ over iminium salts $\mathbf{XII_N}$ by about 184 kJ mol^{-1}.[27] Interestingly, in the phosphorus series $\mathbf{XIII_P}$ is only 50 kJ mol^{-1} more stable than $\mathbf{XII_P}$.[28] Moreover, although diamino carbocations $\mathbf{XIII_N}$ adopt a planar structure ($\mathbf{XIII_NA}$) due to the 3-center-4π-electron system, it was predicted that in the phosphorus series a similar planar structure $\mathbf{XIII_PA}$ would not even be a minimum on the potential energy surface.[25,29] Instead it was found theoretically that only one phosphorus center would be planar, while the second would be pyramidalized ($\mathbf{XIII_PB}$) (Fig. 8). This is due to the electropositivity of the phosphino groups, which shifts a surplus of electron density to the central atom, preventing the π-donation and therefore the planarization of the second phosphorus atom.

Combining these theoretical data, and the observed reactivity of methylenephosphonium salts $\mathbf{XII_P}$, it became clear that diphosphino carbocations $\mathbf{XIII_P}$ could rearrange by a cascade-stabilizing process into their cyclic valence isomers $\mathbf{XIV_P}$ (Fig. 9). Indeed, we hypothesized that the planar phosphorus atom of $\mathbf{XIII_PB}$, resulting from the donation of one phosphorus lone pair to the central carbon, would be highly electrophilic, and that the pyramidalized phosphorus center would act as an internal nucleophile, resulting in the formation of $\mathbf{XIV_P}$. Strikingly, $\mathbf{XIV_P}$ would feature a phosphorus–carbon ylidic bond as shown in $\mathbf{XIV_PA}$, and therefore would be a cyclic carbanionic valence isomer of the diphosphino carbocation $\mathbf{XIII_P}$!

Having previously shown that the stable [bis(diisopropylamino)phosphino](silyl)carbene **4**[30] reacts with trimethylsilyl trifluoromethane sulfonate to form the phosphino carbocation **5**,[26a] a similar synthetic strategy was adopted to prepare the desired heterocycle of type $\mathbf{XIV_P}$, using the bis(diisopropylamino)phosphenium salt as electrophile (Scheme 2). Indeed, $\mathbf{14_P}$ was obtained and isolated in 66% yield as extremely air sensitive white crystals (melting point 89–90 °C).



Scheme 2.

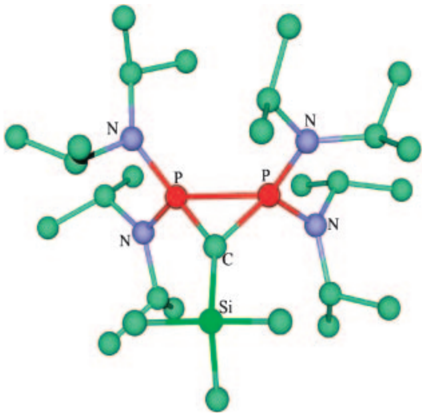


Fig. 10. Molecular view of $\mathbf{14_P}$ in the solid state.

A triplet in the ^{29}Si NMR spectrum suggested the presence of two magnetically equivalent phosphorus nuclei. However, the three-membered ring structure was not clearly suggested by ^{31}P NMR since the signal appeared at much lower field than expected (δ_P +7.3).[18] Fortunately, the ^{13}C NMR signal corresponding to the carbon bonded to the two phosphorus atoms appears at 49.6 ppm, a chemical shift at far too high field for a carbocationic center, but well within the range expected for a carbanion. A single-crystal X-ray diffraction analysis (Fig. 10) clearly demonstrated the cyclic structure of $\mathbf{14_P}$.

The analysis of the electron densities of each of the constituents of the model compound $\mathbf{14'_P}$, (SiH_3 and NH_2 instead of

$SiMe_3$ and $N(i\text{-}Pr)_2$, respectively) performed using ab initio calculations, is of particular interest (Fig. 11).

Each diaminophosphenium unit carries approximately a +1 charge, whereas the carbon bears indeed a −1.6 charge [−1.2 in the σ-space and −0.4 in the (formal) p-orbital]. This view is corroborated by the chemical reactivity of **14$_P$**. For example, methyl magnesium bromide does not react at the carbon center but at phosphorus, leading to the corresponding P-methyl phosphorus ylide in near quantitative yield (Scheme 3).

To complete this study, it was of interest to attempt the preparation of the acyclic valence isomer **XIII$_P$**, in other words an analog of amidinium salts **XIII$_N$**. We first performed calculations, to understand the influence of the phosphorus and carbon substituents on the relative stability of **XIII$_P$** and **XIV$_P$**.[29] The most important result was that the replacement of $Ni\text{Pr}_2$ and Me_3Si groups of the experimentally observed compound **14$_P$** by NH_2 and H_3Si substituents reversed the order of stability: the acyclic isomer came to the fore by $24\,kJ\,mol^{-1}$. The only reasonable explanation for this phenomenon was that the steric demand in the linear form is larger than in the cyclic system. We prepared a variety of precursors with different substituents at P, but were forced, by the synthetic route used at that time, to retain the trimethylsilyl group at carbon (the starting materials being phosphino trimethylsilyl carbenes). With small substituents, such as phenyl, at one of the P centers, the cyclic isomers **XIV$_p$** were not formed, but neither were the desired acyclic compounds of type **13$_P$**. The latter rearrange via 1,3-shift of a P-substituent to the other phosphorus atom giving the isomeric phosphaalkenes **15$_P$**, which are much lower in energy (Scheme 4).[31] Note that the transient formation of **13$_P$** was, however, shown by a trapping experiment.

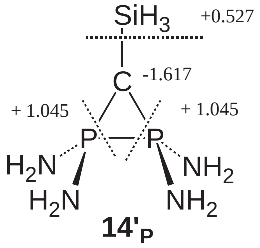
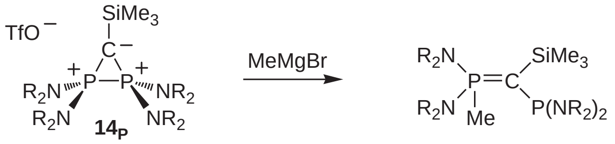


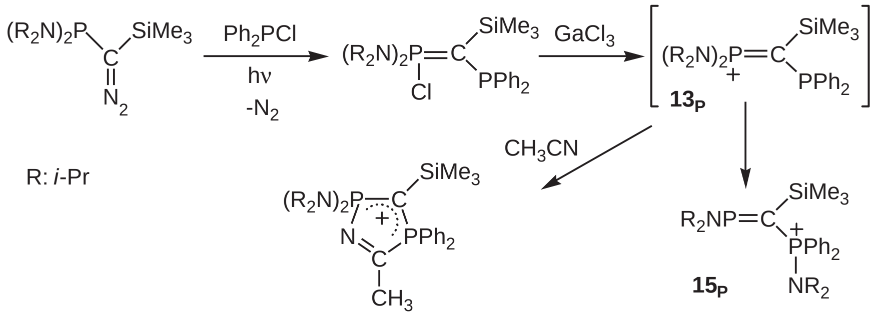
Fig. 11. Charges of the different fragments showing the carbanionic nature of **14'$_P$**.

According to the above discussion, a decrease of the steric hindrance at P favors the open form **XIII$_P$** over its cyclic isomer **XIV$_P$**, but favors also the 1,3-migration of a phosphorus substituent giving **XV$_P$**. We decided therefore to design a novel synthetic route, which would allow the placement of bulky substituents at both phosphorus atoms, but also the reduction of the size of the C-substituent: H was the best candidate.

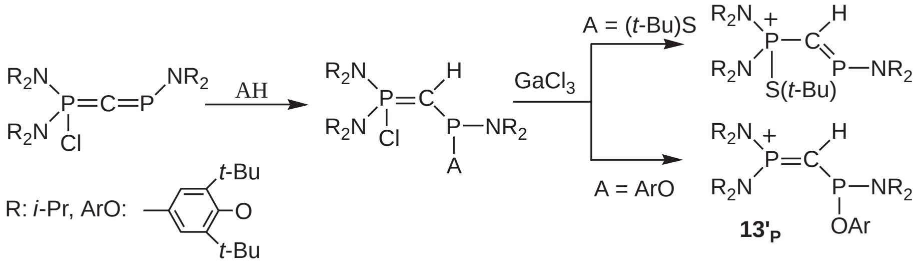
We found that the recently discovered $1\sigma^4,3\sigma^2$-diphosphacumulene[32] cleanly reacted with acidic compounds of type A-H including the bulky *tert*-butylthiol and 4-methyl-2,6-di-*tert*-butylphenol to afford P-chloro ylides (Scheme 5).[33] Abstraction of chloride with gallium trichloride from the thio-substituted ylide quantitatively afforded again a phosphonio phosphaalkene, but when the precursor featuring the (even more bulky) aryloxy group was used, the desired acyclic cation **13'$_P$** was observed. This compound is stable for several weeks in dichloromethane at −20 °C, but it decomposes in few minutes above 0 °C preventing its isolation and an X-ray diffraction study. The ^{31}P NMR chemical shifts are in the range for a bis(diisopropylamino)methylenephosphenium salt and an (amino)(aryloxy)(alkyl)phosphine, which shows, as predicted



Scheme 3.



Scheme 4.



Scheme 5.

XVI **XVII** **XVIII** **XIX**

Fig. 12. Butadiene **XVI** and its valence-isomers.

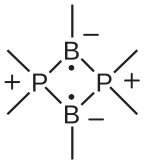
by calculations, that this diphosphino carbocation features a localized double bond involving the bis(amino)-substituted phosphorus, and a single bond to the (amino)(aryloxy)phosphine. In other words, the molecule is presumably highly unsymmetrical, the phenoxy-substituted phosphorus centre remaining pyramidal.

These results, as a whole, were a reiteration that the unique electronic properties of heavier main group elements will allow for the preparation of a variety of new structural moieties that are difficult or impossible to access in the corresponding carbon and nitrogen series. Moreover, the rearrangement of derivatives **XIII$_{\rm P}$** into their cyclic valence isomers **XIV$_{\rm P}$** is a unique example of a transformation of a carbocationic center into a carbanionic center. However, with the help of heavier main group elements, numerous examples can be imagined.

Stable Singlet Diradicals by Valence Isomerization of Boron/Phosphorus Analogs of Butadienes

After the successful discovery of **14$_{\rm P}$**, we looked for new possible valence-isomers unattainable with first row elements. We turned our attention to butadiene **XVI**. Two valence isomers, namely cyclobutene **XVII** and bicyclo[1.1.0]butane **XVIII** were well known, but interestingly the diradical isomer **XIX** had never been isolated (Fig. 12). Indeed, even in the triplet state, 1,3-cyclobutanediyls **XIX**$^{\rm T}$ had only been observed in matrices at very low temperature,[34] although the combination of the two unpaired electrons, leading to bicyclo[1.1.0]butane **XVIII**, is impeded by a huge ring strain and a spin barrier. The corresponding singlet diradicals **XIX**$^{\rm s}$, formally resulting from the homolytic cleavage of the endocyclic σ-bond of **XVIII**, were predicted only as transition states for the inversion of **XVIII**.[35] Optimizing the substituent effects, Abe et al. had been able to spectroscopically observe a few localized carbon-based singlet diradicals,[36] but even today, the half-life in solution at room temperature of the most persistent, is only in the microsecond range.[36e] Obviously, the instability of singlet diradicals **XIX** is due to the very favored ring closing reaction leading to bicyclic isomers **XVIII**.

From this analysis, it became clear that the only way to increase the lifetime of singlet diradicals was to slow down, or better, to prevent the ring-closing process. Towards this end, we decided to investigate the effect of electrostatic repulsion between two negative charges, and therefore to use boron-centered radicals.[37] In order to obtain a molecule which was overall neutral, two positively charged centers were necessary. We chose phosphonium fragments, since in addition to the positive charge, they feature energetically low-lying σ^* orbitals. Indeed, it was known that the presence of such orbitals favored the singlet state and even increased the stability of the corresponding carbon-base diradicals, by allowing through-bond interaction of the two radical sites.[38] Therefore, the target was diradical **XIX$_{\rm P}$** (Fig. 13).



XIX$_{\rm P}$

Fig. 13. Targeted diradical **XIX$_{\rm P}$**.

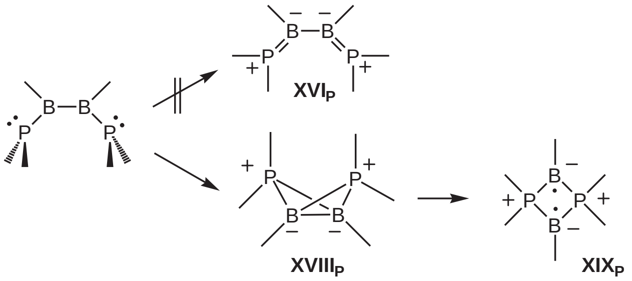
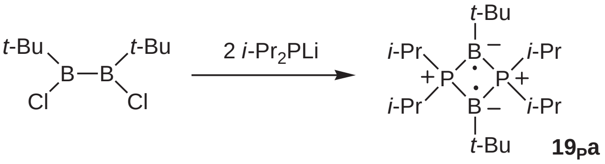


Fig. 14. Projected synthetic route to **XIX$_{\rm P}$**, via valence-isomerization of a 1,2-diphosphinodiborane.



Scheme 6.

Our synthetic strategy was based on the results described above: di(phosphino) carbocations **XIII$_{\rm P}$** adopt a cyclic form **XIV$_{\rm P}$** due to the reluctance of phosphorus to become planar and to form π-bonds. By analogy, it was reasonable to believe that 1,2-diphosphinodiboranes should adopt a bicyclo[1.1.0]-butane form **XVIII$_{\rm P}$**, and hopefully the diradical structure **XIX$_{\rm P}$**, rather than a butadiene-like structure **XVI$_{\rm P}$** (Fig. 14). In other words, we hypothesized that the phosphorus Lewis base centers would interact with the boron Lewis acid centers in position β, rather than α. Note, that the valence isomerization of butadienes into bicyclo[1.1.0]butane derivatives had already been predicted computationally and postulated experimentally in the case of heavier main-group element containing derivatives.[39]

To obtain the desired 1,2-diphosphinodiborane precursors, two equivalents of lithium diisopropylphosphide were added to 1,2-dichloro-1,2-di(*tert*-butyl)diborane, and we were pleased to obtain the desired diradical **19$_{\rm P}$a** in 68% yield as extremely air-sensitive but highly thermally stable yellow crystals (melting point 212 °C) (Scheme 6).[40]

The X-ray diffraction analysis (Fig. 15) revealed the PBPB four-membered ring structure of **19$_{\rm P}$a**. The ring is perfectly planar; the B atoms are in a planar environment (as observed in boron-centered radicals)[37] and the P–B bond lengths (1.89 Å) are equal, but a little shorter than expected for single bonds. The most striking feature was the B–B distance (2.57 Å), which indicated that the B–B bond has been cleaved. Indeed, this value is about 38% greater than that of the longest B–B bond reported so far (1.86 Å).[41] All of these geometric parameters suggested that **19$_{\rm P}$a** was a diradical.

Our own calculations,[40,42] carried out on the parent compound **XIX$_{\rm P}$** (H atoms at phosphorus and boron centers)

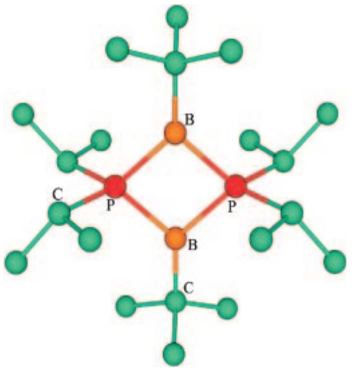


Fig. 15. Molecular view of diradical **19_{Pa}** in the solid state.

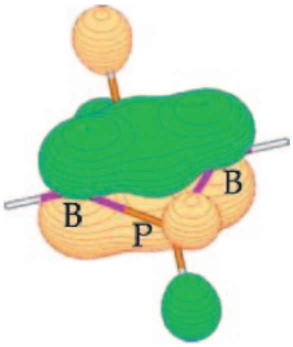


Fig. 16. HOMO of the parent compound **XIX_P**, showing the through-space and through-bond interactions.

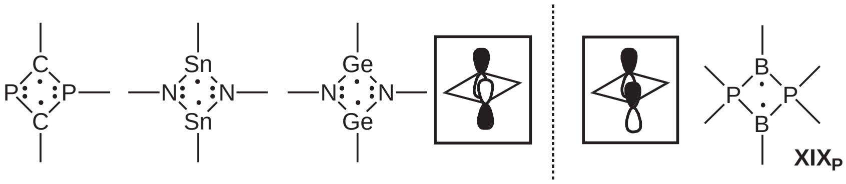
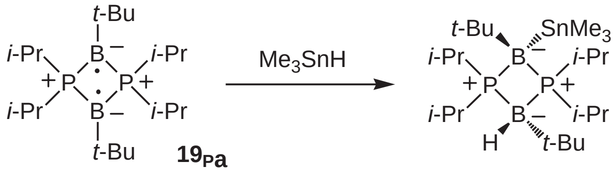


Fig. 17. Stable diradicals with trans-annular anti-bonding π-overlap (left), versus **XIX_P** with trans-annular bonding π-overlap (right).



Scheme 7.

showed that the singlet state is lower in energy than the triplet state by 17.2 kcal/mol, suggesting an interaction between the two radical sites. The nature of the coupling of the two radical sites (positive p-orbital overlap) was apparent from the highest occupied molecular orbital (HOMO) (Fig. 16). It involves the participation of the σ^*(P–C) orbitals, which indicates some through-bond interaction, and an overlap of the 2p(B) orbitals, despite the long boron–boron distance, that suggests some through-space interaction.

Both the through-bond and through-space interactions explain the unusual stability of this species, but also leads to the question: is **19_{Pa}** a true diradical or merely a compound featuring a very long boron–boron π-bond without B–B σ-bond? Cramer et al.[43] concluded that since the value of the singlet–triplet gap calculated for **19_{Pa}** is fairly close to the known S–T splitting of *meta*-benzyne, the appellation "diradical" may be as warranted for **19_{Pa}** as it is for the *meta*-aryne. In addition to the S–T splitting, they evaluate, as a diagnostic, HOMO and LUMO occupation numbers from two-electron-in-two-orbital generalized valence bond calculations, and found 1.81 and 0.19 for **19_{Pa}** (perfect diradicals are characterized by occupation numbers of 1.0 in each orbital, while perfectly closed-shell systems have HOMO and LUMO occupation numbers of 2.0 and 0.0, respectively). Obtaining very similar numbers, Head-Gordon and Jung[44] and Hu and Cheng[45] concluded that **19_{Pa}** should be considered a "diradicaloid" species, and a compound with "a through-space π-bond," respectively! Therefore, the conclusion to this dilemma is clear-cut: this is semantic! Importantly, compound **19_{Pa}** chemically behaves as a diradical as shown, for example, by a clean and spontaneous reaction with trimethyltin hydride at room temperature (Scheme 7).[46] This reaction, which occurs without radical initiators, leads to the trans 1,3-adduct, ruling out a concerted 1,2-addition.

The existence of the trans-annular bonding B–B π-overlap differentiates diradicals of type **XIX_P** from all the other stable diradicals reported so far. Indeed, 2,4-diphosphacyclobutane-1,3-diyls of Niecke et al.[47] and Yoshifuji et al.,[48] as well as the 1,3-diaza-2,4-distannacyclobutane-2,4-diyl of Lappert et al.[49] and 1,3-diaza-2,4-digermacyclobutane-2,4-diyl of Power et al.,[50] feature a trans-annular anti-bonding π-overlap (Fig. 17).

Consequently, according to Woodward–Hoffmann rules, the disrotatory ring closure is thermally forbidden for these diradicals. This has been confirmed by the observation of the photochemically induced ring closure of Niecke's diradical into the corresponding bicyclo[1.1.0]butane isomer.[47a] In contrast, the trans-annular bonding π-overlap in 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls **XIX_P** allows for the thermal ring closure into the bicyclo[1.1.0] valence isomer **$XVIII_P$**. Therefore, a variation of the phosphorus and boron substituents strongly influences the ground-state structure of compounds **$XVIII_P$/XIX_P**. This offered an opportunity not only to isolate the structural extremes, but also to mimic the whole reaction profile for the inversion of **$XVIII_P$**.[51] Without going into details, Figure 18 clearly shows the influence of the substituents on the geometry of the resulting molecule.

These results prompted us to investigate the possibility of preparing a compound for which both isomers of types **$XVIII_P$** and **XIX_P** would be observable. This leads to the concept of "bond-stretch isomerism," introduced by Stohrer and Hoffmann in 1979 using strained tricyclic hydrocarbons:[52] "In the

R	*i*-Pr	*i*-Pr	Ph	Et	Ph
R'	*t*-Bu	Dur	*t*-Bu	Dur	Ph
B-B (Å)	2.57	2.24	1.99	1.89	1.83
τ (°)	180	130	118	115	114

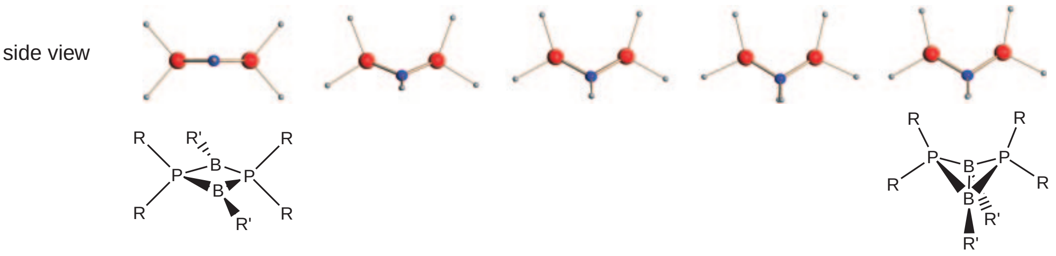


Fig. 18. Influence of the nature of the P and B substituents of the boron–boron bond distance and folding angle in derivatives **18$_\text{P}$**/**19$_\text{P}$** (Dur: 2,3,5,6-tetramethylphenyl).

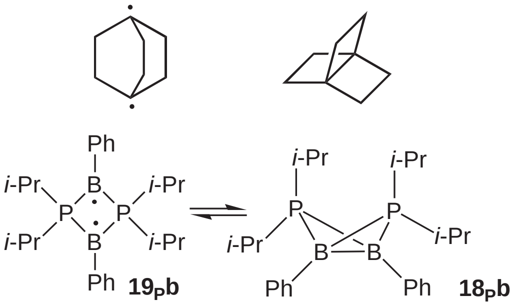


Fig. 19. The two stretch-isomers used by Stohrer and Hoffmann to illustrate the concept (top), and the compounds we used experimentally (bottom).

2,2,2-system the optimum alignment for through-bond coupling of radical lobes creates the conditions for a new type of isomerism—two stable conformations related by a simple bond stretch. These are the normal tricyclic form and the diradical” (Fig. 19, top). Before our work, no experimental evidence for the co-existence of two bond-stretch isomers featuring a trans-annular bonding π-overlap was reported,[53] although, as mentioned above, Niecke's diradicals can be photolytically converted into their stretched bicyclic isomer. In the case of the (i-Pr$_2$PBPh)$_2$ derivative, we have demonstrated, by variable temperature NMR and UV–vis experiments, the existence in solution of an equilibrium between the bicyclo[1.1.0]butane **18$_\text{P}$b** and its 1,3-bora-2,4-diphosphoniocyclobutane-1,3-diyl **19$_\text{P}$b** bond-stretch isomer (Fig. 19, bottom).[54] We have determined experimentally and confirmed by calculations that the free energy difference (ΔH) between the stretch isomers **18$_\text{P}$b** and **19$_\text{P}$b** is about 5.8 kJ mol^{-1} (**19$_\text{P}$b** being the most stable isomer), and that $\Delta S = 30.1 \pm 6.7\,\text{J mol}^{-1}\,\text{K}^{-1}$. Therefore, the order of stability of the bond-stretch isomers, **19$_\text{P}$b** and **18$_\text{P}$b**, is strongly entropy driven. The diradical isomer with the coplanar phenyl group possesses fewer degrees of freedom than the bicyclic isomers in which free rotation of the phenyl groups and inversion at boron are both allowed. This is certainly a unique example of a reaction in which the breaking of a σ-bond is induced by decreasing the temperature, and the bond formation is entropically favored.

After this rather fundamental study, we turned our attention to possible applications of stable singlet diradicals. Indeed, catenation of singlet diradicals, via appropriate linkers, is predicted to lead to antiferromagnetic low-spin polymers, in which the half-filled electron bands would confer the capability for metallic conduction without doping.[55] For this purpose, carbon-based tetraradical prototypes have already been prepared by several different research groups, but conclusions have been difficult to draw due to the instability of such species.[56] We have shown that the coupling of two 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl units of type **XIX$_\text{P}$** via the antiferromagnetic *para*-phenyl linker results in the formation of a tetraradical (Fig. 20), which in the solid-state features boron atoms in a planar environment, very long B–B distances (2.568 Å), and two almost planar PBPB four-membered rings, coplanar with the phenyl ring.[57] In marked contrast, when the ferromagnetic *meta*-phenyl coupling unit was used to link the same two 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls, bicyclic forms were observed for the PBPB fragments. This compound features PBPB cores strongly deviating from planarity (interflap angle between the two PBB units 120.7 and 123.6°), short B–B bond lengths (1.875 and 1.906 Å), and the phenyl linker perpendicular to the PBPB skeletons. The striking differences observed between the solid-state structures of these two derivatives, in addition to a colorless bis(bicyclo[1.1.0]butane), and a deep violet tetraradical, have been explained by a weak “communication” between both diradical sites through the antiferromagnetic linker. Calculations have corroborated this conclusion,[57] but the exact nature of the communication between the two diradical sites of the tetraradical is still under investigation.

The availability of diradicals that can be handled under standard laboratory conditions should lead to further insight into their chemical and physical properties. It raises the likelihood of practical applications, especially in the field of molecular materials such as electrical conductors. Moreover, it is noteworthy that the B–B distance between **19$_\text{P}$b** [257 (exp), 258 pm (calcd)] and **18$_\text{P}$b** [186 pm (calcd)] varies by 40%. Combined with the temperature-dependent interconversion phenomenon, these results open interesting perspectives for “molecular muscles” as well as electrical switch devices.

Conclusion

The influence of heavier main group elements on the rela-

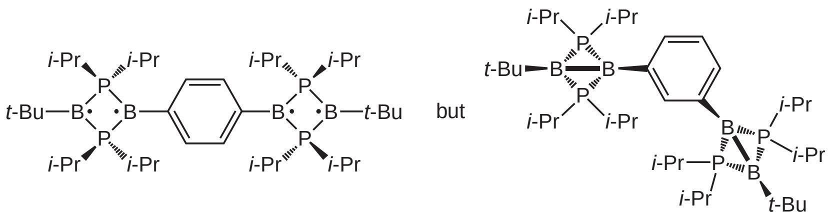


Fig. 20. Depending on the nature of the linker, the coupling of two identical diradical units, leads either to a tetraradical (left), or a bis(bicyclic) derivatives (right).

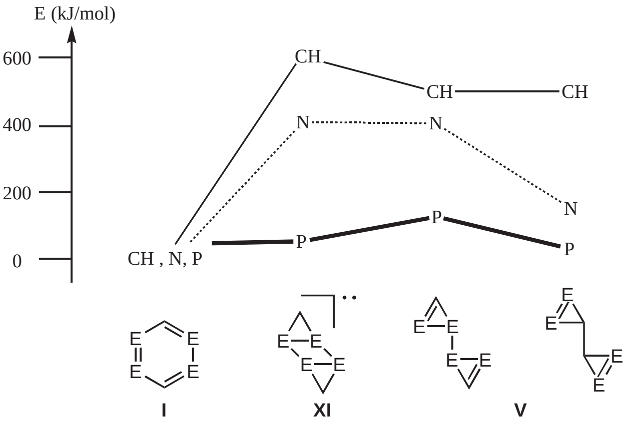


Fig. 21. Influence of the nature of E (CH, N, P) on the relative stability of various valence bond isomers of benzene and hetero analogs.

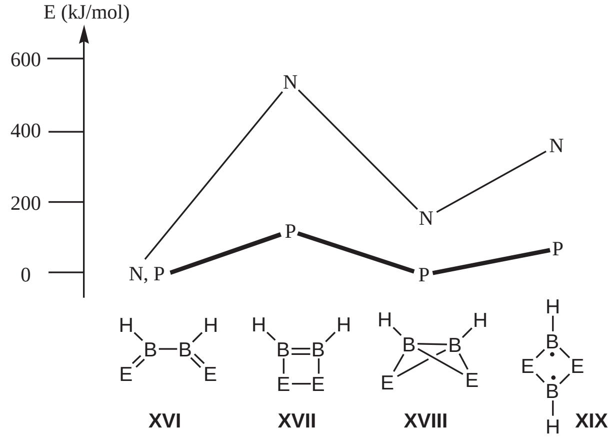


Fig. 23. Influence of the nature of E (NH_2, PH_2) on the relative stability of various butadiene valence isomers.

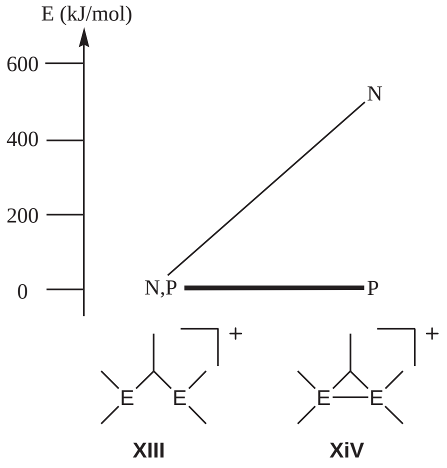


Fig. 22. Influence of the nature of E (N, P) on the relative stability of valence bond isomers **XIII** and **XIV**.

tive stability of various valence bond isomers is well illustrated by the results collected in Figs. 21–23.

In the carbon series the *anti*-tricyclohexylene **XI**, which is best described as a singlet biradical, is calculated to be only 84 kJ mol^{-1} in energy above the known bicycloprop-2-enyl **V**, but 608 kJ mol^{-1} above benzene![14] In the phosphorus series, a totally different trend is observed since the tetraphosphabenzene $\mathbf{I_P}$ and the "π^*–π^*" valence isomer $\mathbf{XI_P}$ have almost the same energy (Fig. 21).[58]

Calculations predict[25,29] that in the nitrogen series the parent amidinium salt $\mathbf{XIII_N}$ is 541 kJ mol^{-1} more stable than the cyclic valence isomer $\mathbf{XIV_N}$, which therefore cannot be prepared. In marked contrast, in the phosphorus series, the difference in energy between the open and closed forms $\mathbf{XIII_P}$ and $\mathbf{XIV_P}$, is only a few kJ mol^{-1}. Slight changes in the nature of the substituents bring one or the other isomer to the fore (Fig. 22).

Lastly, Figure 23 shows that for hetero-butadiene valence isomers, the diradical structure is certainly not isolable using nitrogen instead of phosphorus. Indeed, calculations predict the BNBN diradical to be some 350 kJ mol^{-1} higher in energy than its butadiene isomer.[42]

The synthesis of $\mathbf{11_P}$, $\mathbf{14_P}$, and $\mathbf{19_P}$ suggests that the unique electronic properties of heavier main group elements will allow for the preparation of a variety of new structural moieties that are difficult or impossible to access in the corresponding carbon and nitrogen series.

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