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Group 15 biradicals: synthesis and reactivity of cyclobutane-1,3-diyl and cyclopentane-1,3-diyl analogues

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Readily accessible group 15 biradicals of the type $[E(\mu\text{-NR})]_2$ (E = P–Bi) form planar 6π-electronic-4-membered heterocycles featuring open-shell singlet biradical character. They can be utilized to activate small molecules bearing single, double and triple bonds as well as to trap labile *in situ* generated fragments. In the reaction with CO and R–NC (R = small alkyl or aryl substituent) pnictogen analogues of cyclopentane-1,3-diyl are formed which represent robust molecular switches. Group 15 biradicals with two different radical sites display regioselectivity upon addition of small molecules.

Introduction

Main group chemistry takes a central place in the development of new synthesis approaches by utilizing innovative concepts, enabling the generation of compounds that chemists would consider not accessible based on generally accepted views and past experience. Amongst these concepts are the utilization of bulky substituents to introduce kinetic stabilisation,[1–18] weakly coordinating anions,[19–28] as well as unusual reaction media,[29] such as ionic liquids,[30–35] neat (Brønstedt and Lewis) acids (*e.g.* SO_2,[36,37] oleum[38,39]) and bases (*e.g.* NH_3).[40–45] But also approaches such as application of N-heterocyclic carbenes,[46–54] frustrated Lewis acid/Lewis base pairs (FLPs),[55–58] adduct formation[59] with bulky very strong Lewis acids (*e.g.* $B(C_6F_5)_3$)[60–63] as well as sophisticated high-temperature synthesis methods combined with matrix isolation techniques[64,65] have led to the isolation of highly reactive (ionic or neutral) fragments as well as to the activation of small molecules, which was originally known only from transition metal chemistry. Furthermore, low-valent main group species[66] with open coordination sites, persistent radicals[66] and biradicals,[67–70] or main group compounds with multiple bonds[9] can be used as transition metal mimics for the activation of small molecules, which was first brought forth by P. P. Power.[71]

This frontier article focuses only on the recent development in the synthesis and reactivity of group 15 biradicals and zwitterions as well as their application. The general theory,[72–74] synthesis and classification of (main group) biradicals[67–70] have been reported extensively in a series of superb reviews and shall not be repeated here. Nevertheless, it seems appropriate to start with a short word on the history of (bi)radicals and the notation biradical.

Radicals, pseudoelements, biradicals, diradicals, biradicaloids?

The term radical was derived from the Latin word for root *radix* (*radicalis*, *cf.* radish) and appeared first in the 17th century in some European languages and meant "going to the origin".[75] In chemistry it has been used – even before the discovery of the electron – since the middle of the 19th century to describe chemical units, which do not change upon chemical transformations such as a methyl or ethyl group, following the idea of a periodic table of elements but for organic moieties.[76] The chemistry of radicals began at the beginning of the 20th century when Gomberg reported on the triphenylmethyl radical.[77] The first paramagnetic biradical was isolated by Schlenk in 1915 when he treated bis-diphenyl-benzyl dichloride with a copper-tin alloy affording a persistent biradical.[78] Ever since (bi)radicals have been in the focus of research, although some chemists[79] avoided using the term (bi)radical (*e.g.* for $^{\bullet}CN$, $^{\bullet}OCN$, $^{\bullet}N_3$ *etc.*) in the early years after the discovery and favoured the term "pseudoelement" (*e.g.* pseudohalogen).[80]

According to IUPAC,[81] we call a compound a biradical (synonym diradical) when it is an "even-electron molecular entity with two (possibly delocalized) radical centres which act nearly independently of each other". The term biradicaloid (synonym diradicaloid) often refers to a subset of biradicals with two radical centres interacting significantly. Taking the interaction between the two radical sites into consideration,

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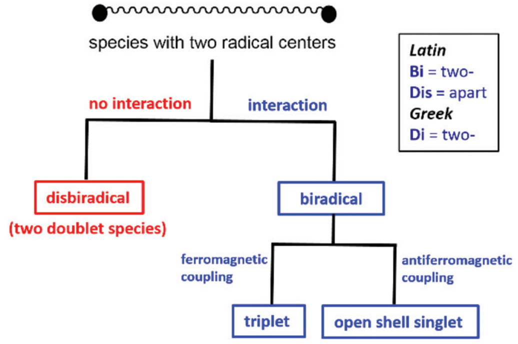


Scheme 1 Definition for biradicals and disbiradicals used in this article.

either a two-doublet species (almost no coupling) or a triplet arises in the case of a ferromagnetic, or an open-shell singlet species with an antiferromagnetic coupling (Scheme 1). To use a consistent (Latin based) notation, we suggest to use disbiradical (= "true" biradical rather than biradical or diradical) for the two-doublet species and for all other cases biradical. Since there is no defined limit for the degree of interaction, there is no need to use the term biradicaloid unless theory suggests a clear distinction. Indeed, with respect to interaction, the transitions between biradical → biradicaloid → closed-shell singlet species are fluid.[70]

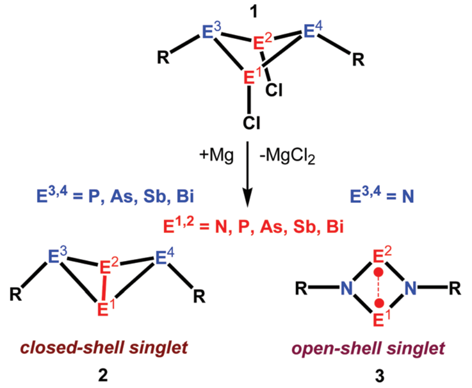
Throughout the article, the following notation was used: **Z** for a general species (Z = number), **ZR** for a general species with a specific substituent R, and **ZR_E** (E = pnictogen = E^1 = E^2) as well as **ZR_E^1_E^2** for a species with a specific R and element of group 15 (E, E^1, and E^2).

Group 15 analogues of cyclobutane-1,3-diyls

Preliminary remarks

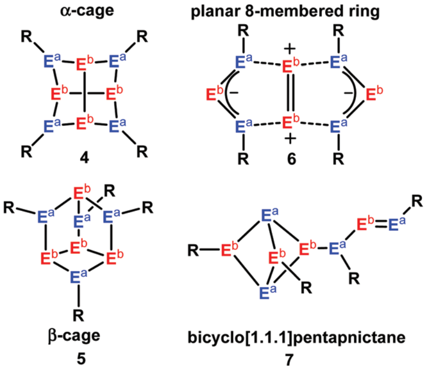
A true milestone in main group as well as biradical chemistry was the discovery of Niecke's 1,3-diphospha-cyclobutane-2,4-diyl which was published in 1995. The reactivity of 1,3-diphospha-cyclobutane-2,4-diyls has been studied in depth by the Niecke group[82] and later by Ito *et al.*, who introduced air-tolerant 1,3-diphospha-cyclobutane-2,4-diyls, which were obtained by direct arylation.[83,84]

We have been interested in the preparation of cyclobutane-1,3-diyl analogues of the type $[E^1(\mu\text{-NR})_2E^2]$ (**3**) containing exclusively group 15 elements ($E^{1,2,3,4}$ = pnictogen, Scheme 2). As shown in Scheme 2, upon reduction of $[ClE^{1,2}(\mu\text{-}E^{3,4}R)]_2$ (**1**) either a planar 4-membered heterocycle (**3**), featuring open-shell biradical character, is formed or a closed-shell, non-planar butterfly species (**2**) with a *trans*-annular bond. Both species represent singlet species, that is, the spin density is precisely zero at each and every point in space (*i.e.* both are NMR active but EPR silent). However, open-shell means that at least two Slater determinants are needed to describe the wave function properly (*vide infra*). When a bond is formed across the ring, a puckered butterfly molecule (**2**) is obtained exhibiting no radical character at all. Interestingly, according to computation, when $E^{3,4}$ is a nitrogen atom, always the planar 6π-electronic biradical **3** is energetically favoured, while in all other cases the bicyclic closed-shell butterfly species **2** represent the only minima at the energy surface. Such butterfly species (**2**), for example with four phosphorus atoms,[85] have been known for more than 30 years featuring a normal *trans*-annular covalent bond.[86]



Scheme 2 Closed-shell (**2**) *versus* open-shell singlet $[E^1(\mu\text{-NR})_2E^2]$ (**3**) species.

What is the origin of these structural and electronic differences? Three things are important: the first point is a better delocalisation of the 6π electrons in case of nitrogen, which favours a planar situation as found for **3**.[87–90] The second point, and this was brought to attention by Ugalde *et al.*, is the fact that the angle strain in case of the nitrogen species is decreased in the planar structure, since the nitrogen prefers a wider bond angle. Hence, the angle strain is not compensated for the E^1–E^2 σ bond formation across the ring as found in the butterfly structure **2** (Scheme 2).[91] As nitrogen is substituted by heavier pnictogen atoms (P–Bi), the bond angle strain is decreased, a *trans*-annular bond is formed and the butterfly compound **2** becomes the most stable isomer.[86] Furthermore, Ugalde *et al.* stated "aromaticity does not play any role in the stabilization of the planar isomers",[91] in contrast to our findings.[87–90] The third point involves kinetic stabilisation. When a small substituent is used, oligomerisation – mainly dimerization – occurs, leading to the formation of various types of dimers, as depicted in Scheme 3.[89,90,92] Therefore, to prevent the 4-membered biradical **3** from oligomerisation, kinetic protection (*e.g.* by a terphenyl = Ter = 2,6-bis(2,4,6-trimethylphenyl)-phenyl, Bbp = 2,6-bis[bis(trimethylsilyl)methyl] phenyl, or hypersilyl = Hyp = bis-tris(trimethylsilyl)silyl) is required. The cone angle[15,16] is a good measure of the steric hindrance introduced by the bulky substituent on the nitrogen atom. It decreases, for example, along the series 232° (terphenyl), 230° (Bbp) to 213° (hypersilyl) group.[2] The smallest cone angle to kinetically stabilise biradical **3** is about 200°. Even for the hypersilyl substituted biradical **3Hyp**, dimerisation slowly occurs in polar solvents (yielding the α-cage dimer **4Hyp** as



Scheme 3 Known closed-shell singlet dimers of $[E^b(\mu\text{-}E^aR)]_2$ biradicals (a = 1,2; b = 3,4 see Scheme 2, for **7** dimer of $[E^b(\mu\text{-}E^aR)(\mu\text{-}E^bR)E^b]$).

depicted in Scheme 3), but can be suppressed, when non-polar solvents are used.[89,90] Moreover, the charge transfer of the substituent into the 4-membered ring plays a vital role for the reactivity. For example, it increases for $[P(\mu\text{-}NR)]_2$ (**3R_P**, R = Ter, Bbp, and Hyp) from the terphenyl (0.4e) to the hypersilyl (1.2e) substituted species, which is the most reactive species amongst these three compounds.

Synthesis und structure of cyclo-1,3-dipnicta-2,4-diazane-1,3-diyls

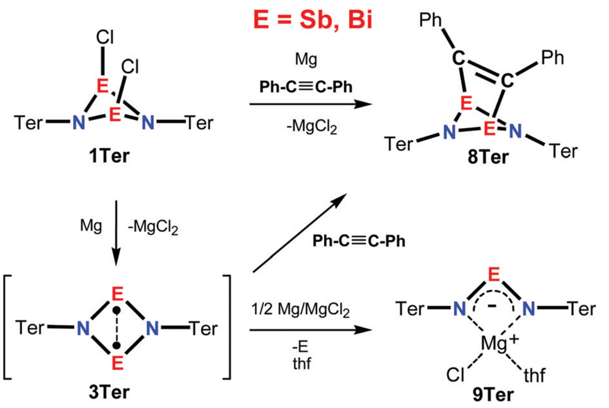
There are several ways to synthesise pnictogen-centred biradicals of the type $[E(\mu\text{-}NR)]_2$ (**3R_E** with E = P, As; R = Ter, Bbp, Hyp, and Trityl).[87,88,90,93] As starting material either 1,3-dichloro-cyclodipnictadiazanes $[ClE(\mu\text{-}NR)]_2$ (**1R_E** in Scheme 2) or the acyclic species $RN(ECl_2)_2$, which forms *in situ* $[ClE(\mu\text{-}NR)]_2$ and ECl_3 upon reduction, can be used. The best reducing agent seems to be magnesium chips so far. In both cases, it is possible to isolate the phosphorus- and arsenic-centred biradical **3R_E** in almost quantitative yield (>90%).[87,89,93] Activation of Mg, which is sometimes necessary due to passivation, is achieved either by stirring in an argon atmosphere or by adding a drop of mercury (amalgam formation). $[E(\mu\text{-}NR)]_2$-biradicals (**3R_E** with E = P, As; R = Ter, Bbp, Hyp, and Trityl) are thermally stable up to over 200°. For example, the terphenyl substituted species are stable in solution as well as in the solid state. X-ray structure analysis of all $[E(\mu\text{-}NR)]_2$-biradicals (**3R_E**) reveals a planar E_2N_2 heterocycle with E–N distances displaying some double bond character. The *trans*-annular E–E distance is always considerably longer than the sum of covalent radii but much shorter than the sum of the van der Waals radii (Table 1).

For the heavier congeners $[E(\mu\text{-}NR)]_2$ (**3Ter_E** with E = Sb, Bi) the situation is different, as reduction with Mg always leads to the formation of allyl-anion analogues of the type $[R\text{-}NEN\text{-}R]^-$ (Scheme 4, salt **9Ter_E**).[94] Nevertheless, *in situ* generation of the antimony and bismuth biradicals can be proven by reducing the dichloro species $[ClE(\mu\text{-}NR)]_2$ (**1Ter_E**) with magnesium in the presence of diphenylacetylene (tolane, Ph–C≡C–Ph). Indeed, by this approach it is possible to obtain the diphenylacetylene addition products (**8Ter_E**). This approach also works for the arsenic- and phosphorus-centred biradicals **3Ter_E** and is an interesting application of all discussed biradicals **3**, as they easily add reactive intermediates as long as they are small (see the sections on molecule activation and trapping).

Table 1 Computed data of planar $[E(\mu\text{-}NTer)]_2$ (**3Ter_E** with E = P, As, Sb, Bi). Bond lengths in Å, angles in °, β in % and singlet–triplet (ST) gap in [kJ mol^{-1}][a]

E =	P	As	Sb	Bi
E1–N1	1.766	1.903	2.129	2.241
E1···E2	2.721	2.961	3.347	3.530
$\sum r_{cov}(E\text{–}E)$[101]	2.22	2.42	2.80	3.02
$\sum r_{vdW}(E\text{–}E)$[102]	3.60	3.70	4.12	4.14
β[b]	27	34	47	54
ST gap[b]	82	55	25	17

[a] pbe/def2svp geometry. [b] CAS(6,4)/def2svp single point@pbe/def2svp geometry, biradical character $\beta = 2c_2^2/(c_1^2 + c_2^2)$.[74]

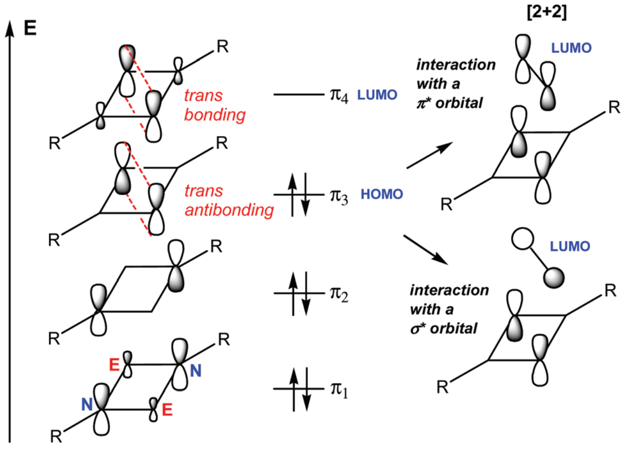


Scheme 4 *In situ* generation of heavy open-shell singlet biradicals $[E(\mu\text{-}NTer)]_2$ (E = Sb, Bi) and their trapping by diphenylacetylene.

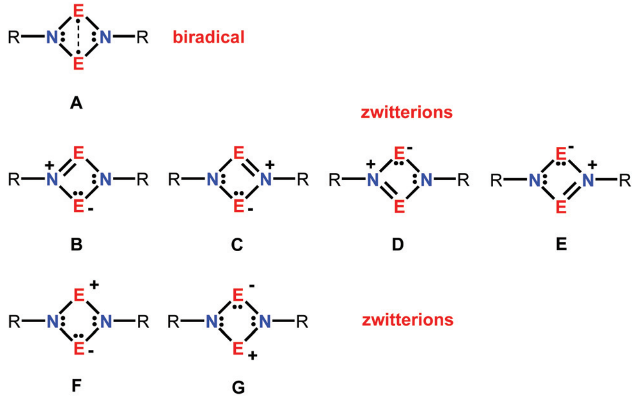
Syntheses of biradical **3** with different radical centres is also possible when either the 4-membered rings $[ClE^1(\mu\text{-}NR)_2E^2Cl]$ (**1R_E¹_E²**, E^1 = P, E^2 = As; R = Ter; Scheme 2) or the acyclic species $Cl_2E^1\text{–}N(R)\text{–}E^2 = N\text{–}R$ (E^1 = P and E^2 = Sb; E^1 = P, As, Sb, Bi and E^2 = N; R = Ter) are available.[95,96] Reduction with either Mg chips or in some cases with KC_8 leads to the formation of stable 4-membered biradicals $[E^1(\mu\text{-}NR)_2E^2]$ (**3Ter_E¹_E²**, E^1 = P, E^2 = As[93] and E^1 = P, As, Sb, Bi with E^2 = N; R = Ter).[87,88,94] In case of $Cl_2Sb\text{–}N(Ter)\text{–}P{=}N\text{–}Ter$ the *in situ* formation of the biradical **3Ter_P_Sb** can be assumed upon reduction as indicated by the products of the trapping reaction with diphenylacetylene (*cf.* Scheme 4, **8Ter_P_Sb**),[97] while without trapping reagent either the $[Ter\text{-}NPN\text{-}Ter]^-$ (**9Ter_P**) or the 8-membered dimer with a *trans*-annular Sb=Sb double bond is isolated, when KC_8 in benzene is used rather than Mg in thf (**6Ter_P_Sb**, Scheme 3). All 4-membered $[E^1(\mu\text{-}NR)_2E^2]$ species (**3**) exhibit planar kite-shaped four-membered E^1NE^2N heterocycles with almost equal E^1–N and E^2–N bond lengths.

Electronic structure – biradical *versus* zwitterion

The electronic situation of the $[E(\mu\text{-}NR)]_2$ biradicals (**3**) resembles that of 6π-electron, aromatic hydrocarbons.[87,88] As depicted in Scheme 5, there are three doubly-occupied molecular orbitals describing the π bond situation. While π_1 is delocalized over the entire 4-membered ring, π_2 and π_4 represent more or less nitrogen or pnictogen (E)-centred orbitals, respectively. In case of aryl-substituted biradicals, π_2 is further delocalised into the aryl substituent, which is not shown in Scheme 5. For the understanding of the biradical character, the HOMO and LUMO are the most important orbitals (Scheme 5). The HOMO is *trans*-annularly antibonding while the LUMO is bonding. Often a simple two electrons in two orbitals CASSCF(2,2) calculation is sufficient to indicate some biradical character. According to Miliordos and coworkers,[73,74] the biradical character β can be estimated by the formula: $\beta = 2c_2^2/(c_1^2 + c_2^2)$ (closed-shell molecule: $c_2 = 0$, $\beta = 0$; pure biradical: $c_2 = c_1$, $\beta = 1$) using the coefficients of the two considered reference determinants $c_1|\pi_1^2\pi_2^2\pi_3^2>$ and $c_2|\pi_1^2\pi_2^2\pi_4^2>$ (Scheme 5 left), which amounts for example to *ca.* 27% for the $[P(\mu\text{-}NTer)]_2$ biradical (**3Ter_P**, Table 1). This value corresponds to an occupation of the nonbonding π_3 orbital with 1.7 electrons and π_4 with about 0.3 electrons, therefore featuring a certain degree of covalent bonding across the ring. Also NRT (NRT = natural resonance theory)[98,99] computations for the model compounds **3Ph_E** display a significant contribution of a Lewis representation exhibiting two unpaired electrons (*ca.* 50%, Scheme 6, **A**) besides zwitterionic representations (**B–G**). Salem *et al.* pointed out that a biradicalic state always (if the overlap integral between both radical sites $S_{AB} > 0$) contains a certain degree of zwitterionic besides covalent character and *vice versa*, that is, concepts such as biradical or zwitterion represent a simplification of the actual situation and are two sides of the same coin. The zwitterionic situation might even be considered as a *trans*-annular FLP (Scheme 6, Lewis representations **F** and **G**) contributing to the often observed remarkable reactivity (*vide infra*).



Scheme 5 Left: Simplified MO description of 4-membered biradicals of the type $[E(\mu\text{-}NR)]_2$ (**3**, E = P–Bi). Right: HOMO (biradical)–LUMO (molecule to be added) [2 + 2] interaction of $[E(\mu\text{-}NR)]_2$ with molecules containing π or σ bonds.

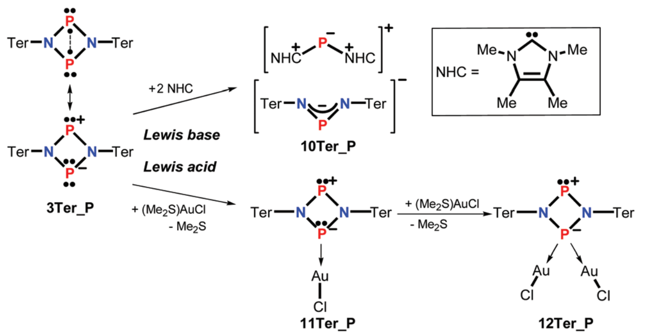


Scheme 6 Biradicalic and zwitterionic VB representations of $[E(\mu\text{-}NR)]_2$ (**3**).

For $[E^1(\mu\text{-}NR)_2E^2]$, the biradical character increases the heavier the pnictogen atoms $E^{1,2}$ = P–Bi (in Table 1 shown for **3Ter_E**),[91,94] but decreases with the introduction of a third nitrogen atom as shown for the cyclic triazenide species $[E(\mu\text{-}NTer)_2N]$ (**3Ter_N_E**^{2} with E^2 = P: 15 > As 10% > Sb 6% > Bi 0%).[100] In the latter cases computations reveal that these N_3E rings represent species at the borderline between singlet biradicals and closed-shell zwitterions with diminished reactivity compared to known singlet biradicals $[E^1(\mu\text{-}NTer)_2E^2]$ (**3Ter_E1_E2** with E^1, $E^2 \neq$ N). For example, triazenide species $[N(\mu\text{-}NTer)_2E^2]$ (**3Ter_N_E**^{2}, E^2 = P–Bi) do not show any addition reactions (*vide infra*).[100]

Reactivity towards Lewis acids and bases

Experimentally, zwitterionic properties of $[E(\mu\text{-}NR)]_2$ biradicals (**3**) can be studied in reactions with either Lewis acids and bases (Scheme 7). For example, in $[P(\mu\text{-}NTer)]_2$ (**3Ter_P**) the Lewis acid should attack the formal P^- and the base the P^+ centre (Scheme 7). Upon addition of a Lewis acid such as $(Me_2S)AuCl$ to the $[P(\mu\text{-}NTer)]_2$ biradical, mono- (**11Ter_P**) as well as diadduct formation (**12Ter_P**) is observed, indicating donor properties.[103] Interestingly, also the second equivalent



Scheme 7 Reactions of $[P(\mu\text{-}NTer)]_2$ (**3Ter_P**) with Lewis acids and bases to demonstrate the zwitterionic character.

of the Lewis acid attacks the same P atom. Streubel and Frontera studied several Lewis acid complexes of [E(μ-NR)]$_2$ biradicals (**3**) by means of computations. They figured out that in some cases the biradical character increases dramatically upon complexation.[104]

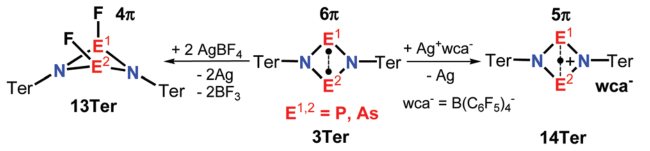
When a neutral base such as an *N*-heterocyclic carbene (NHC) is added to the [P(μ-NTer)]$_2$ biradical (**3Ter_P**, Scheme 7), a very fast reaction occurs and within a minute quantitative transformation to give an NHC-stabilized phosphorus cation [(NHC)$_2$P$^+$] and a terphenyl-stabilized [Ter-NPN-Ter]$^-$ anion (salt **10Ter_P** in Scheme 7).[103] Also anionic bases can be used to formally cut out a "P$^+$" from the [P(μ-NTer)]$_2$ biradical (**3Ter_P**) as can be seen in the reaction with two equivalents of [R$_4$N]$^+$CN$^-$ affording an ammonium salt of the type [R$_4$N]$^+$[NC–P–CN]$^-$, bearing the dicyanido-phosphide ion, in addition to [R$_4$N]$^+$[TerNPNTer]$^-$.

Oxidation – radical cations of the type [E^1(μ-NTer)$_2$E^2]$^{+\bullet}$

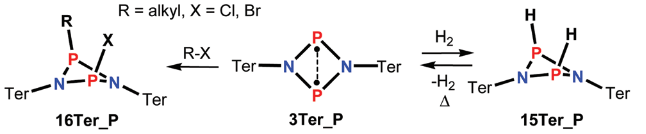
Biradicals of the type [E^1(μ-NTer)$_2$E^2] (**3Ter**, E^{1,2} = P, As) can easily undergo a one-electron-oxidation (Scheme 8) utilizing for example silver salts of weakly coordinating anions (wca$^-$) such as [AgL$_3$][B(C$_6$F$_5$)$_4$] (L = donor solvents) to afford persistent cyclic radical cations, [E^1(μ-NTer)$_2$E^2]$^{+\bullet}$(**14Ter**). When smaller and more basic anions are employed, the anions are found to form covalent bonds to the radical centres, yielding dipnictadiazanes, *e.g.* [F-E^1(μ-NTer)$_2$E^2-F] (**13Ter**) in the reaction with AgBF$_4$. Computational and EPR data reveal that the spin density is almost completely localized at the two heavier pnictogen centres E^{1,2}. The bonding situation in the radical cations **14Ter** features a rare example of a *trans*-annular, one-electron π bond without having a σ bond. Selected examples of radicals centred on phosphorus can be found in the literature.[105,106]

Activation of small molecules

Due to the unusual bonding situation with two unpaired electrons, which do slightly interact, [E(μ-NR)]$_2$ species **3** feature a special reactivity and can be used to activate bonds in small molecules bearing single, double and triple bonds.[90,107–109] In terms of MO theory, this reactivity can be attributed to the *trans*-annularly antibonding HOMO of biradical **3**, which can interact with empty σ* (*e.g.* H$_2$, NH$_3$) or π* (alkynes, alkenes) LUMOs of the molecule to be activated (Scheme 5 right). While [E(μ-NR)]$_2$ (E = P, As) and [P(μ-NR)$_2$As] (R = Ter, Bbp, and Hyp) can be prepared in bulk,[87–90] the heavier congeners only have fleeting existence in solution,[94] but once prepared *in situ*, they can also be used for the activation of small molecules (*vide supra*, Scheme 4).



Scheme 8 Reactions of [E^1(μ-NTer)$_2$E^2] (**3Ter**) with silver salts to isolate radical cations [E^1(μ-NTer)$_2$E^2]$^{+\bullet}$ (**14Ter**). Weakly coordinating anions have to be used as counter ions. 4π electrons localized at the N atoms (one lone pair for each N) and one lone pair (in a sp$^\lambda$ hybrid orbital) at each E atom not shown for clarity.

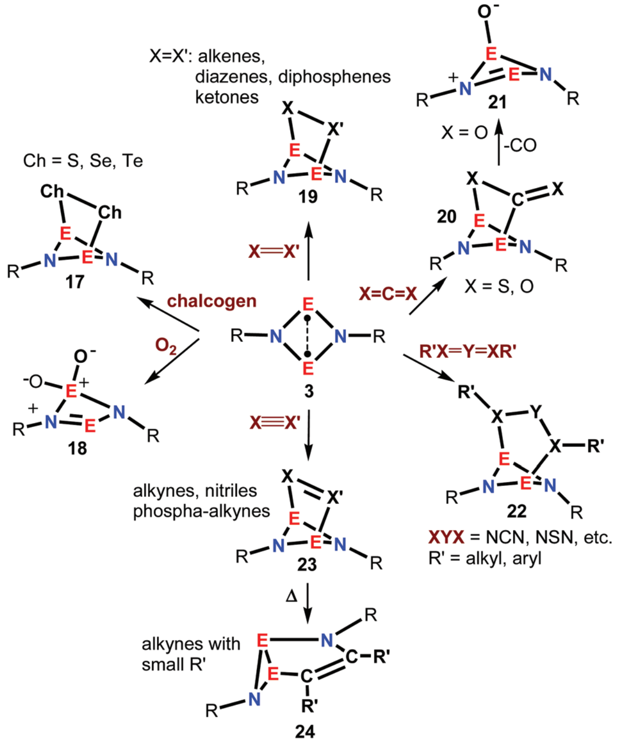


Scheme 9 Reactions of [P(μ-NTer)]$_2$ (**3Ter_P**) with dihydrogen (right) and molecules containing an alkyl halogen bonds (left).

Molecules, containing a single bond. Molecular dihydrogen adds easily to [P(μ-NTer)]$_2$ (**3Ter_P**) and almost quantitatively at low temperature affording the exclusive formation of the non-planar *cis*-isomer [H–P(μ-NTer)]$_2$ in an exergonic process (**15Ter_P**, Scheme 9 right). It is interesting to note that the addition of dihydrogen is reversible, that is, at temperatures above 60 °C dihydrogen is released recovering the biradical besides dihydrogen.[108] Also molecules of the type R–X (R = alkyl, X = Cl, Br) react instantly with **3Ter_P** to give the addition product **16Ter_P** (Scheme 9 left).

Moreover, the [P(μ-NTer)]$_2$ biradical (**3Ter_P**) reacts readily with all chalcogens yielding in case of S, Se and Te cage compounds (**17**) with a dichalcogen bridge (Scheme 10).[87,88,90,93,110] These reactions are usually quantitative. Interestingly, the sulphur reaction is rather fast and complete within minutes, while the reaction with selenium takes several hours. The reaction with tellurium takes about 14 days at 60 °C. The reaction with molecular oxygen is also very fast in solution but rather slow in the solid state. In both cases only one phosphorus atom is oxidised and carries two oxygen atoms (compound **18**). This leads to one tetracoordinated P$^{(V)}$ atom with P–N single bonds and one dicoordinated P$^{(III)}$ atom with P–N bonds with some multiple bond character as illustrated in Scheme 10.

Molecules, containing a localized double bond (alkenes, diazenes, diphosphenes, and ketones) or delocalized resonance-stabilised π bonds such as in conjugated dienes, CS$_2$, CO$_2$, sulphurdiimides and carbodiimides react fast and in almost quantitative yields affording bicyclic cage compounds (Scheme 10) either with a diatomic (species **19** and **20**) or triatomic (R-NSN-R, R-NCN-R) bridges (**22**) depending on the electronic situation.[87,88,90,93,110] Once the double bond containing molecule is added, the E$_2$N$_2$ ring becomes non-planar and the *trans*-annular E–E distances are even slightly shorter although there is no E–E covalent bonding. It is maybe interesting to note that in case of conjugated dienes always a formal [2 + 2] cycloaddition is observed but no [4 + 2] product. Furthermore, in some cases (*e.g.* dimethyl butadiene) the addition is reversible at slightly elevated temperatures under vacuum. In case of the addition reaction of CS$_2$, only the [2 + 2] addition product is observed yielding a [2,1,1]bicyclic product (**20_CS$_2$**) with an exocyclic C=S double bond. However, contrary to the reaction with CS$_2$, CO$_2$ is reduced by the biradical, yielding CO and a P$_2$N$_2$ ring with one oxidized P atom in a two-step process (species **21** in Scheme 10). Again



Scheme 10 Reactions of $[E(\mu\text{-NR})]_2$ (**3**) with molecules bearing single, double and triple bonds. All these reactions were carried for $[P(\mu\text{-NTer})]_2$ (**3Ter_P**). Similar reactions were found for all **3R_E^1_E^2** (R = Ter, Hyp, and Bbp; $E^{1,2}$ = P, As).

the HOMO–LUMO interaction results in the formation of a CO-bridged cage compound as isolated for the CS_2 addition product (**20_CO$_2$**), which decomposes with the release of CO in a slightly exergonic process, affording a mono-oxidized product $[OP(\mu\text{-NTer})_2P]$ (**21**).[108]

Molecules, containing a triple bond, are also easily activated by $[E(\mu\text{-NR})]_2$ (**3**, E = P, As) forming [2.1.1]bicyclic structures in almost quantitative yields at ambient temperatures as depicted in Scheme 10 (species **23**).[90,94,109–112] For example, in the case of acetylene, diphenylacetylene or bis(benzothio)acetylene, [2 + 2] addition products can be isolated in bulk by this approach. Structural analysis of **23** showed that the E_2N_2 ring becomes puckered and the C–C bond elongated upon addition, now being in the range of a typical double bond. The *trans*-annular E–E distances are rather short although there is no bonding interaction. Interestingly, with a small substituent at the alkyne, such as R = H, the addition product (**23**, [2.1.1]bicyclus) rearranges slowly upon thermal treatment to afford a [3.1.0]bicycle (species **24** in Scheme 10),[113] which is not observed for bulky substituents (*e.g.* R = Ph). X-ray structural elucidation reveals that the alkyne is inserted into the E_2N_2 ring, forming first a six-membered heterocycle, which is also a pnictogen-centred biradical. But in this case a *trans*-annular covalent bond is formed, affording **24** with a three-membered dipnicta-aziridine and a condensed planar 5-membered ring, which lies almost perpendicular to the 3-ring.

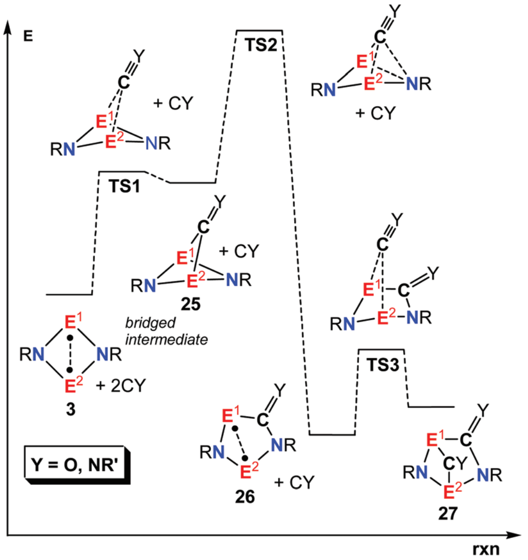
Group 15 analogues of cyclopentane-1,3-diyls

Accidental discovery

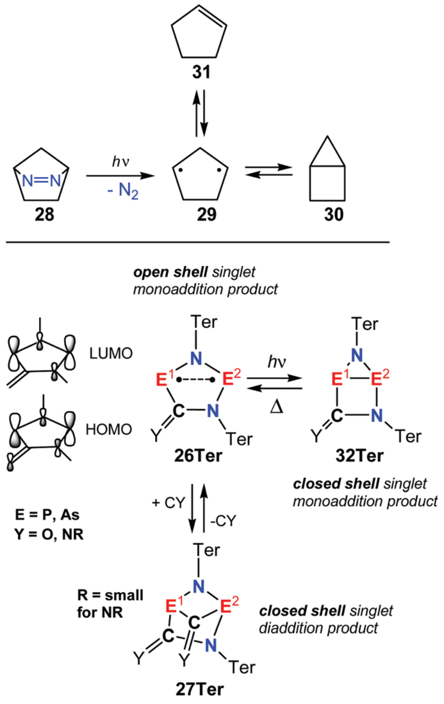
In the course of the reactivity study of $[P(\mu\text{-NTer})]_2$ (**3Ter_P**) towards unsaturated compounds, we also deployed carbon monoxide, a molecule with a triple bond. CO only adds completely to $[P(\mu\text{-NTer})]_2$ (**3Ter_P**) dissolved in benzene, when a CO pressure of 60 bar is applied, affording a mono-addition product **26** (Scheme 11).[114] X-ray diffraction studies allowed the unequivocal identification of **26.** Astonishingly, in contrast to the alkynes, the CO molecule reacts in a [2 + 1] fashion, forming an intermediate **25** (*via* TS1), which also inserts the CO into the 4-membered E_2N_2 ring (*via* TS2) but only at the carbon atom. Finally, this insertion leads to the formation of a five-membered heterocycle (**26**_CO), a deep-red cyclopentane-1,3-diyl analogue (Scheme 11), which is also a pnictogen-centred biradical. In a slightly endergonic process, a small amount of a closed-shell diaddition product (**27**_CO) can be observed, which, however, easily decomposes upon CO pressure release, thus hampering isolation.[114]

Pnictogen-centred cyclopentane-1,3-diyls: synthesis and application as molecular switches

Red crystals of the CO-monoaddition biradical (**26Ter_CO**, Schemes 11 and 12) become colourless upon UV irradiation. ^{31}P NMR studies reveal the formation of a new species under irradiation. In agreement with computations, two new high-field shifted signals are observed with a rather small P–P coupling, which is characteristic of the formation azadiphosphiri-



Scheme 11 Qualitative energy profile for the reaction of $[E^1(\mu\text{-NR})_2E^2]$ with CY (Y = O, NR′). Isolated systems: Carbonyl (Y = O): monoaddition products **26**. **27** only observed and studied for E^1 = E^2 = P and R = Ter. Isonitrile (Y = NR′): monoaddition product only for R = Ter and R′ = Dmp: $E^{1,2}$ = P; E^1 = P, As and E^2 = N, As. Mono- and diaddition products for R = Ter, Hyp and R′ = small *e.g.* ^{t}Bu.



Scheme 12 Top: Parent cyclopentane-1,3-diyls (**29**) and its conversion. Bottom: Heteroatomic substituted analogue (**26Ter**) as molecular switch. Known pnictogen-housane systems: $E^{1,2}$ = P, As and E^1 = P and E^2 = As for R = *t*-Bu, Dmp.

dines, clearly indicating the formation of a housane-type product, now exhibiting a *trans*-annular P–P bond (**32Ter** in Scheme 12).[114] Attempted isolation of the colourless housane product **32Ter** failed due to intrinsic thermal reverse transformation of the housane into the biradical **26Ter** within an hour at ambient temperature in an exothermic reaction. Such behaviour can be referred to as a photochromic molecular switch.[115–117] Housane formation is known from the organic parent species (Scheme 12, **29** → **30**). In contrast to the parent biradical **29**, the biradicalic pnictogen analogue **26Ter** is stabilized by delocalisation of the six π electrons. Therefore, the housane **32Ter** is thermodynamically less stable compared to biradical **26Ter**, while for the parent cyclopentane-1,3-diyl **29** such a stabilisation is not possible (Scheme 12), and thus housane **30** as well as rearrangement product **31** are more stable.

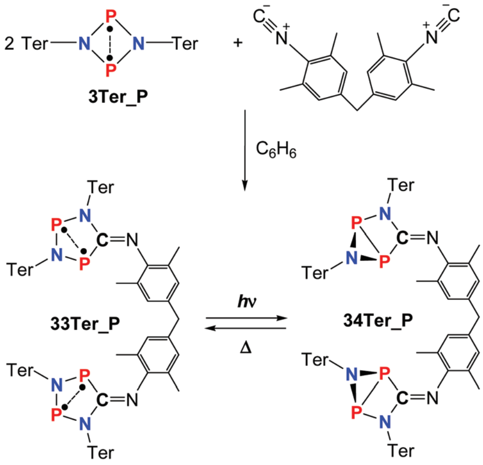
Isonitriles show similar electronic properties to CO, but allow tuning of the electronic and size properties by different substitution. Indeed, isonitriles display the same type of addition reaction as found for CO (Scheme 12).[118] For example, bulky terphenyl-substituted isonitrile does not react at all with $[P(\mu\text{-NTer})]_2$ (**3Ter_P**) but the smaller dimethylphenyl (Dmp) isonitrile forms exclusively the deep blue monoaddition product **26Ter_P**_Dmp, while in case of the *t*-butyl isonitrile mono- and diaddition product formation can be observed (**26Ter_P**_*t*-BuNC and **27Ter_P**_*t*-BuNC, Schemes 11 and 12). With a large excess of *t*-Bu-NC, the colorless double addition product **27Ter_P**_*t*-BuNC can be isolated. Interestingly, upon dissolving of colorless diaddition product **27Ter_P**_*t*-BuNC, a green solution is formed, which according to NMR studies features three species that coexist in solution: the colorless diaddition product **27Ter_P**_*t*-BuNC, the blue monoaddition product **26Ter_P**_*t*-BuNC, and the orange starting material $[P(\mu\text{-NTer})]_2$ (**3Ter_P**) along with *t*-Bu-NC (Scheme 11).[118]

Similar to the 4-membered biradicals $[E^1(\mu\text{-NR})_2E^2]$, the frontier orbitals of the pnictogen analogues of cyclopentane-1,3-diyls display a LUMO, strongly localized on both pnictogen atoms in a bonding fashion but antibonding around the NE^1NE^2 moiety, and the HOMO antibonding between both E atoms (Scheme 12). Therefore, increasing the population of the LUMO upon irradiation leads to a *trans*-annular $E^1\cdots E^2$ bonding situation, finally resulting in the formation of a housane in a disrotatory ring closure.[118,119] Usually, upon irradiation also the mostly red or blue coloured crystals become colourless and crack, which causes large problems in the X-ray diffraction experiments. In the case of the mixed P/As cyclopentane-1,3-diyl (**26Ter_P_As**_DmpNC, Scheme 12), this isomerisation does not cause the crystals to completely fall apart. Hence, two data sets can be collected from a single crystal: a first data set at the beginning and a second after 12 hours of X-ray irradiation. While in the first data set, the planar 5-membered biradical **26Ter_P_As**_DmpNC is dominant, in the second data set, 95% occupation is found for the housane species **32Ter_P_As**_DmpNC.[119]

Interestingly, cyclopentane-1,3-diyl derivatives of the type **26Ter_N_E**_DmpNC, containing an N_3 unit, can also be generated by the reaction of triazenide species $[E(\mu\text{-NTer})_2N]$ (**3Ter_N_E**, E = P, As) with DmpNC (Scheme 11).[119] But like their 4-membered counterparts (*vide supra*), they feature strongly polarized E–N bonds, a rather small biradical character and therefore are better referred to as zwitterions, which is also manifested by their inability to activate molecules.

Catenation

By employing a bifunctional isonitrile in the reaction with $[P(\mu\text{-NTer})_2N]$ (**3Ter_P**), it is possible to link two biradical centres (**33Ter_P**, Scheme 13).[118] To ensure a similar reactivity compared to DmpNC, which exclusively forms the 5-membered biradical (**26Ter_P**_Dmp, Scheme 12), methylene-bis(dimethyl)phenyl-isonitrile, featuring comparable structural and electronic properties, can be used. Both starting materials, $[P(\mu\text{-NTer})_2N]$ and the diisonitrile, can be combined as solids. Upon addition of benzene as solvent at ambient temperatures, the formation of a blue solution is observed after less than 30 minutes, from which dark blue block-shaped crystals of **33Ter_P** can be isolated (*ca.* 60–80%, Scheme 13).[118] Interestingly, with respect to the C=N-double bond of the inserted isonitrile group, there are three isomers of the tetraradical possible (*Z*,*Z*; *Z*,*E*; *E*,*E*). In solution only two, namely the *Z*,*Z* and *Z*,*E* isomers can be detected in the ratio 9 : 1 as indicated by the ^{31}P NMR studies. As desired, UV light induced housane formation is observed, both mono- as well double-



Scheme 13 Catenation of phosphorus-centred cyclopentane-1,3-diyls featuring molecular switch properties.[118]

housane formation (**34Ter_P**, Scheme 13). Again the thermal reverse reaction leads to formal tetraradical formation (**33Ter_P**). The ground state for tetraradical **33Ter_P** is an open-shell singlet state. Owing to the long bridging unit, which results in quasi-degenerate MOs for the orbitals localized on each of the five-membered rings, and since the delocalised double bond system is fragmented by the methylene group, there is no coupling between the two cyclopentanediyl moieties. Thus the electron exchange integral is essentially zero. Formal tetraradical **33Ter_P** shows a similar activation chemistry as discussed before for [P(μ-NTer)$_2$N] (**3Ter_P**, Scheme 10).[118]

Regioselective addition reactions

All of the biradicals discussed with two different radical sites or a different chemical environment for both radical sites, such as [E^1(μ-NR)$_2$E^2] (**3R_E^1_E^2**) and all pnictogen centered 5-membered cyclopentane-1,3-diyls (**26R_E^1_E^2**), exhibit regioselectivity upon adding XY (X ≠ Y) molecules bearing single, double and triple bonds (Scheme 10). For example, treatment of [P(μ-NTer)$_2$As] (**3Ter_P_As**) with CS_2 always leads to the formation of two isomeric [2.1.1]-bicyclic species (**20Ter_P_As**_CS_2, Scheme 10) in the ratio 7 : 1, always favouring P–C and As–S over P–S and As–C bond formation.[93] Or complete regioselectivity is observed in the reaction of *t*-Bu–C≡P with [P(μ-NTer)$_2$As] (**3Ter_P_As**), yielding exclusively the P–C and As–P bridged addition product (**23Ter_P_As**_*t*-Bu–CP). Also the insertion of isonitriles R–NC (R = small alkyl or aryl) in [P(μ-NTer)$_2$As] (**3Ter_As_P**) are highly regioselective, yielding mostly the As–C(NR)/NC(NR) bonded 5-membered biradicals (**26Ter_As_P**_RNC, Scheme 12). Interestingly, according to computations, all cyclopentanediyl derivatives **26**, in which E^2 is heavier than E^1 (Scheme 12), are thermodynamically more stable than the observed species, in which E^1 is heavier than E^2, due to kinetic protection provided by the two terphenyl substituents.[119]

Conclusion and outlook

Heteroatom-substituted cyclobutanediyl analogues **3R_E^1_E^2** are planar 4-membered biradicals of the type [E^1(μ-NR)$_2$E^2] (E^{1,2} = pnictogen, R = bulky substituent = Ter, Bbp, Hyp) and have electronic structures that are related to those of aromatic hydrocarbons, which have six π electrons and therefore formally obey the Hückel rule. However, triazenide species [N(μ-NTer)$_2$E^2] (**3R_N_E^2**: E^2 = P–Bi) feature a zwitterionic bond situation rather than a large biradical character, contrary to the situation found in [E^1(μ-NR)$_2$E^2] (E^{1,2} = P, As, Sb, Bi). The latter biradicals can be used to activate molecules bearing single, double or triple bonds. Especially, [P(μ-NTer)]$_2$, [As(μ-NTer)]$_2$ and [P(μ-NTer)$_2$As] are suitable for further studies as they are chemically very robust and can easily be prepared in bulk. They can even be used to trap highly labile molecules (*e.g.* Ph–P═P–Ph)[120] and radicalic fragments (*e.g.* HO$^•$)[121] as well as for the generation of pnictogen cage compounds.[94,109] Furthermore, it remains to be demonstrated that [E(μ-NR)]$_2$ biradicals might be utilized as catalysts in (metal free) hydrogenation reactions, for example.

Ring expansion reactions of cyclobutanediyls [E^1(μ-NR)$_2$E^2] with isonitriles enable the synthesis of group 15 derivatives of cyclopentane-1,3-diyl (**26R_E^1_E^2**) featuring N_P, N_As, P_P or P_As atoms as radical centres within the 5-membered heterocycle. However, there are limitations to this insertion reaction, and the preparation of cyclopentane-1,3-diyls, bearing N_Sb, As_As, or P_Sb radical centres, still remains a challenge. Especially, the phosphorus-centred biradical **26Ter_P**_DmpNC (Scheme 12) is readily available. Dependent of the bulkiness of the isonitrile, another equivalent of isonitrile can be incorporated, affording [2.1.1]-heterobicycles (*e.g.* **27Ter_P**_*t*-BuNC). The high reactivity of pnictogen-centred cyclopentane-1,3-diyls can also be studied in reactions with molecules bearing multiple bonds. Upon irradiation, the reversible formation of housane type species **32** is observed, a behaviour, which is known from molecular switches. Future studies should include kinetical aspects, quantum yields and application of pnictogen-centred cyclopentane-1,3-diyl analogues (**26**) as molecular switches. It is also interesting to see if these cyclopentane-1,3-diyl analogues can be tuned with respect to the bulkiness of the R substituent in the isonitrile CN-R and the radical sites. Also investigations of the electronic properties by introducing electron-withdrawing or -donating groups with the aim to generate a molecular switch, which works on visible light or even infrared irradiation, is of broad interest. Moreover, it can be assumed that cyclopentane-1,3-diyl based switches can be used for switching chemical reactions, *e.g.* the addition of isonitriles.

Finally, the open-shell-singlet-biradical concept is often viewed as contentious since there are no definitive spectroscopic experiments to prove the existence of open-shell singlet biradicals (unless there is a very low-lying triplet state). However, there are indicators, which can be derived from theory as well as from experiments. Theoretically derived indicators are: (i) a restricted Hartree–Fock → unrestricted

Hartree–Fock wave function instability, that is, no closed-shell wave function is found, (ii) a small singlet–triplet gap (ΔE_{S-T}), (iii) a β value >20%, and (iv) biradicalic and zwitterionic Lewis representations in the valence bond description, *e.g.* obtained from NRT computations. Experimentally, elongated bonds, unusual chemistry (molecule activation such as reversible H_2 addition, trapping properties), and molecular switch behaviour are often observed. Besides, such biradicals can readily be oxidized to give persistent radicals or reduced to afford anions. Furthermore, biradicals usually feature also a small splitting between their lowest energy and first excited singlet states (ΔE_{S1-S0}), which is associated with a long-wave-length absorption in the UV/vis spectrum.[70] The latter aspect plays an essential role when it comes to molecular switch properties as found for the pnictogen-centred cyclopentane-1,3-diyl analogues.

Conflicts of interest

There are no conflicts to declare.

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