P,N Biradicaloids

[P(µ-NTer)]₂: A Biradicaloid That Is Stable at High Temperature**

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In memory of Kurt Dehnicke

As early as 1894 Michaelis and Schroeter isolated the first phosphorus(III)–nitrogen heterocycle from the reaction of aniline hydrochloride with an excess of PCl₃ (Scheme 1).^[1] Interestingly, the authors assumed to have isolated the monomeric species, C_6H_5 –N=P–Cl, which they called "phosphazobenzene chloride" but already speculated on the existence of the dimer. Today we know that the dimer is the stable form, and such four-membered rings of the type [XP(μ -NR)]₂, which contain alternating phosphorus(III) and nitrogen centers, are called *cyclo*-1,3-diphospha(III)-2,4-diazanes (X = halogen, R = organic group; old name: 1,3-diaza-2,4-diphosphetidines).^[2] They play a major role in preparative phosphorus–nitrogen chemistry because such species are good starting materials for polycyclic inorganic and organometallic compounds.^[3,4]



Scheme 1. Synthesis of 1,3-dichloro-2,4-diphenyl-*cyclo*-1,3-diphospha-(III)-2,4-diazane.

Cyclo-1,3-diphospha(III)-2,4-diazanes (1) can exist as *cis* or *trans* isomers with trigonal-pyramidal P and trigonal-planar N atoms.^[3] Both the N and the P atoms have one localized lone pair. Thus, formally eight electrons are found for this type of electron-rich heterocycles (Scheme 2). To the best of our knowledge, four-membered P₂N₂ rings bearing 6 π electrons are unknown. As illustrated in Scheme 2, three possible target molecules (2, 3, and 4) with electronic structures that are related to those of aromatic hydrocarbons ([4*n*+2] π electrons),^[5] can be considered. The most promising candidate for synthesis seemed to be the neutral *cyclo*-1,3-

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Scheme 2. Four-membered heterocycles with alternating N and P^{III} atoms bearing 6π electrons derived from cyclo-1,3-diphospha(III)-2,4-diazanes.

diphospha-2,4-diazane biradicaloid, $[P(\mu-NR)]_2$ (**3**; R = bulky group) which should formally be generated in a twoelectron reduction process upon chloride ion abstraction. Different reducing reagents, such as lithium metal, $[Cp_2Ti-(btmsa)]^{[6]}$ (btmsa = bis(trimethylsilyl)acetylene, Me₃Si-C= C-SiMe₃) with the reactive {Cp₂Ti^{II}} fragment concelled in the η^2 -bounded btmsa complex, and $[{Cp_2Ti^{III}Cl}_2]$ were utilized. Furthermore, it was of interest to study the effect of the bulky group on the reduction process. Thus, the terphenyl (Ter = 2,6-Mes₂-C₆H₃, Mes = 2,4,6-Me₃C₆H₂)^[7] and hypersilyl group (Hyp = (Me₃Si)₃Si)^[8] were used for kinetic stabilization.

Following our interest in Group 15 heterocycle chemistry,^[9] we describe herein the synthesis, isolation and full characterization of a formal aromatic P_2N_2 heterocycle of the type $[P(\mu-NR)]_2$ (R = Hyp, Ter) with an unusual biradicaloid bond situation.

Biradicals can be described as molecules bearing two unpaired electrons (in two almost degenerate non-bonding molecular orbitals) that act almost independently of each other.^[10] Species in which the two radical centers interact significantly are often referred to as biradicaloids.^[11,12] In contrast to very short-lived radical intermediates of organic reactions, numerous biradicaloids of heavy main-group elements were isolated in the last two decades, some of which formally are intermediates in the σ-bond-formation process.^[12] Pioneering work in this field was carried out by Niecke et al. for $[ClC(\mu-PMes^*)]_2^{[13]}$ (and later for several derivatives), which might be regarded as the isolobal analogues of the well-studied S₂N₂ heterocycle.^[14] Along with these carbonbased 1,3-biradicaloids, a 1,3-dibora-2,4-diphosphacyclobutane-1,3-diyl compound [tBuB(µ-PiPr2)]2 was reported and systematically studied by Bertrand et al.^[15] Isolobal replacement of the nitrogen constituents in S_2N_2 by ER moieties and the sulfur atoms by NR groups leads to isovalence-electronic, experimentally known species $[RE(\mu-NR')]_2$ (E = Group 14 element; $[CISn(\mu-N-SiMe_3)]_2^{[16]}$ and $[RGe(\mu-NSiMe_3)]_2$ (R = 2,6-Dipp₂C₆H₃, Dipp = 2,6-*i*Pr₂C₆H₃)).^[17] Recently, the compound $[RAl(\mu-PtBu_2)]_2$ (R = $PtBu_2$) from Schnöckel et al. extended the area of intermediates of σ -bond-formation processes.^[18]

Using lithium (or magnesium) as reducing agent in the reaction with **1**R (R = Hyp,^[19] Ter^[20]) leads to the unexpected formation of the diazaphosphaallyl system **5**R (Scheme 3, Figure 1) in good yields (>90 %). Such 1,3 diazaphospha-allyl lithium complexes had been discussed by Lappert^[21] and isolated by Niecke et al.^[22] in the reaction of R(H)N–P = N– Aryl (R = CPh₃, 1-Ad, *t*Bu; Aryl = *t*Bu₃C₆H₃)) with *n*BuLi. In the only paper on metal reduction of [XP(μ -NR)]₂ (X = halogen) species, Paine et al. reported the isolation of an eightmembered cage compound P₄(*t*BuN)₄, which is a structural analogue of S₄N₄.^[23] Here the reduction of [CIP(μ -N*t*Bu)]₂ was carried out with magnesium chips and a dimer of the fourmembered heterocycle **3***t*Bu was found (Scheme 2).



Scheme 3. Reduction of 1R (btmsa = $Me_3Si-C=C-SiMe_3$).



Figure 1. ORTEP of the molecular structure of **5**Hyp (left) and **6**Hyp (right) in the crystal. Hydrogen atoms omitted for clarity. Ellipsoids are set at 30% probability at 173 K. Selected bond lengths [Å] and angles [°]: **5**Hyp: Li1–N2 2.01(7), Li1–N1 2.05(6), Li1–P1 2.53(6), N1–P1 1.585(2), N2–P1 1.586(2), P1–N1 Li1 87(2), N1–P1–N2 106.9(1). **6**Hyp: P1–N1 1.742(1), P1–N2 1.723(1), P2–N1 1.733(3), P2–N2 1.739(2), P1–P2 2.442(1), Si1–N1 1.759(1), Si5–N2 1.765(1); N1-P1-N2 83.5(1), P1-N1-P2 89.3(1), P1-N2-P2 89.7(1), P1-N1-Si1 133.6(1), P2-N1-Si1 137.0(1).

Our new method to synthesize 1,3-diazaphosphaallyllithium complexes is fast for 1Ter (< 60 min), but requires 48 h in case of **1**Hyp for a complete conversion (2 mmol).^[24a] To study intermediates, ³¹P NMR spectroscopy experiments were carried out, which revealed for the reduction of 1Hyp (singlet at δ (³¹P) = 257 ppm)^[19] the intermediate formation of biradicaloid **3**Hyp (quintet at $\delta = 334$ ppm with ${}^{2}J({}^{31}P{}^{-14}N) =$ 42 Hz). For the analogous (but fast) reaction with 1Ter, no intermediate but rather the 1,3-diazaphosphaallyl species **5**Ter was observed (**5**Ter: $\delta({}^{31}P) = 357.6$; cf. **5**Hyp: $\delta({}^{31}P) =$ 401.5 and 350–380 Li[R–N–P=N-Aryl] (R = CPh₃, 1-Ad, tBu, $Aryl = tBu_3C_6H_3)$.^[22] Unfortunately, it was impossible to isolate 3Hyp from the reaction mixture, but it led to the idea of using milder reducing agents, such as [Cp₂Ti(btmsa)] and $[{Cp_2TiCl}_2]$. The reaction of $[ClP(\mu-NR)]_2$ with $[Cp_2Ti-$ (btmsa)] yields, depending on the bulky group, either 1) for R = Hyp the btmsa-bridged addition product 6Hyp; or 2) for R = Ter the intriguing four-membered biradicaloid heterocycle 3Ter (Scheme 3). In the latter case the larger Ter group protects biradicaloid 3Ter from addition of the acetylene (btmsa) and from the dimerization observed for R = tBu.^[23] To avoid addition of btmsa to 3Hyp, the reduction was again carried out this time utilizing [{Cp₂TiCl₂], and indeed biradicaloid 3Hyp could be observed. 3Ter can also be prepared when $[{Cp_2TiCl}_2]$ is used as reducing reagent. To show that our assumption of a two-step reaction to 6Hyp when [Cp₂Ti(btmsa)] was used is correct, freshly prepared 3Hyp was reacted with free btmsa, which also afforded 6Hyp as the only product (Scheme 3), while the analogous reaction of 3Ter with btmsa afforded only the starting materials (Scheme 3). Therefore, the kinetic protection is more substantial in 3Ter than in 3Hyp. The larger steric shielding in 3Ter can also be deduced from its reactivity. While 3Ter can be isolated in large quantities and is thermally stable up to 224°C, 3Hyp once formed decomposes quickly in solution, and it is extremely difficult to isolate 3Hyp as a pure

substance. Single-crystal studies of **3**Hyp revealed the correct connectivity, but the poor data set does not allow a detailed discussion. The different reactivity of **3**Hyp in contrast to **3**Ter can also be partly attributed to electronic effects (apart from a larger steric protection in **3**Ter). The electronic interactions with substituents control the extent of biradical character markedly,^[12c] and is increased upon pushing more electron density to the ring system, which is the case in **3**Hyp compared to **3**Ter (cf. charge of the P₂N₂ ring: $\Sigma q(N_2P_2) = -1.22$ and -0.41 e, respectively).^[24bc]

Diazaphosphaallyllithium complex **5**Hyp, btmsa-bridged **6**Hyp, and the biradicaloid **3**Ter were fully characterized by NMR, IR, and Raman spectroscopy, elemental analysis, and single-crystal structure elucidation (Figure 1 and Figure 2).^[24a] Here we will focus on biradicaloid **3**Ter, which is the first neutral all-pnictogen 6 π -electron four-membered heterocycle.

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Figure 2. ORTEP of the molecular structure of **3**Ter in the crystal. H atoms omitted for clarity; ellipsoids are set at 30% probability at 233 K. Selected bond lengths [Å] and angles [°]: N1–C1 1.423(2), N1–P2 1.715(1), N1–P1 1.718(1), P1…P2 2.6186(8); C1-N1-P2 130.8(1), C1-N1-P1 129.6(1), P2-N1-P1 99.44(6), N1ⁱ-P1-N1 80.48(8), N1-P2-N1ⁱ 80.64(8), P2-N1-P1–N1ⁱ 0.0. Symmetry code: (i) -x, y, -z+3/2.

As illustrated in Scheme 3, both synthetic routes with either [Cp₂Ti(btmsa)] or [{Cp₂TiCl₂] as reducing agents afford in good yields (> 80 %) 3Ter as orange microcrystalline solid. Biradicaloid 3Ter is air- and moisture-sensitive but stable under argon atmosphere over a long period as solid and in solvents such as thf, diethyl ether, or toluene, even at ambient temperatures. The orange color of 3Ter vanishes rapidly when traces of H₂O are present. Like 5Hyp and btmsa-bridged 6Hyp, biradicaloid 3Ter is easily prepared in bulk and almost indefinitely stable when stored in a sealed tube. ³¹P NMR spectroscopy in particular is suitable to follow the reduction process and to distinguish between 1Ter $(\delta(^{31}P) = 227.4 \text{ ppm}$ (*cis* isomer), 264.1 ppm (trans isomer)),^[20] and **3**Ter (δ (³¹P) = 289.8 ppm). The characteristic deshielding of the P atoms in central P₂N₂ unit indicates a P₂N π -bonding system. The resonance signals lie in the range typical for cyclic π -delocalized P,N aromatics (cf. Ter-N₄P: $\delta(^{31}P) = 217.2 \text{ ppm},^{[9d]} \text{ Mes}^* - N_4P: \quad \delta(^{31}P) = 226.7 \text{ ppm},^{[9b]}$ $(Me_3Si)_2N-N_3P_2: \delta(^{31}P) = 292.1/317.2 \text{ ppm}),^{[9a]}$ which is considerably more deshielded compared to the compound [Li- $(dme)]_{2}^{+}[Me_{3}Si-C(\mu-P)]_{2}^{2-}$ (δ [³¹P]=200.3) from Niecke et al.^[25] The presence of aromaticity is supported by the calculated $NICS(0)^{[24b,26]}$ value of -6 ppm (cf. -7 ppm for $[Li(dme)]_{2}^{+}[Me_{3}Si-C(\mu-P)]_{2}^{2-},^{[25]} \text{ and } +5 \text{ ppm in } 4\pi \text{ elec-}$ tronic, antiaromatic $[TerN(\mu-Si)]_2$.^[27]

Biradicaloid **3**Ter crystallizes as orange crystals from toluene (or Et₂O) without solvent molecules in the monoclinic space group *C*2/*c* and with four units per cell. The phenyl rings on the amino nitrogen are twisted to each other, with a dihedral angle of 27.63° forming a pocket with four aryl groups (in the 2 and 6 position) in which the N₂P₂ ring is very well sterically protected (Figure 2). Thus, the molecular structure shows, in contrast to P₄(*t*BuN)₄, a monomer consisting of a planar, *C*_s-symmetric four-membered P₂N₂ ring (\neq (P1NP2) = 99.44(6)°, \neq (N1P1N1') = 80.48(8)°, and \neq (N1P2N1') = 80.64(8)°). For comparison a butterfly conformation is found for **1**Ter (\neq (NPNP) = -5.3(1)°) and **6**Hyp $(\not\leq (\text{NPNP}) = -27.3(1)^{\circ})$. Both P-N bonds (1.715(1) and 1.718(1) Å) are almost equivalent and lie in the range found for 1Ter (1.709(2) and 1.731(2) Å), which are shorter than the sum of the covalent radii for a single bond $(d_{cov}(N-P) = 1.8,$ $d_{cov}(N=P) = 1.6 \text{ Å}).^{[28]}$ Significantly shorter bonds are observed in the five-membered tetrazaphospholes Mes*- N_4P (1.631(4) and 1.664(3) Å).^[9b] Comparison of the structural data of 1Ter (cis isomer) with those of 3Ter (Table 1) reveal only small differences. Even the P---P distance is almost identical (1Ter: 2.612(1) vs. 3Ter: 2.6186(8) Å, cf. $\Sigma r_{cov}(P-$ P) = 2.22 Å), indicating no significant transannular interaction. It is interesting to note that the compound $[P(\mu-PMes^*)]_2$ of Fluck et al., which is the isovalence-electronic phosphorus analogue of 3Ter (both N atoms substituted by two P atoms), shows a strong transannular interaction with a P-P distance of 2.166(2) Å and thus must be referred to as a bicyclotetraphosphane.^[29] This major difference can be attributed to the fact that tricoordinated P atoms prefer a pyramidal environment with a lone pair containing a significant amount of s orbital character, while nitrogen atoms prefer a trigonal planar environment when delocalization of the lone pair (occupying a p orbital) is possible.^[24] Thus delocalization of the 6π electrons (N: $2e^-$, P: $1e^-$) stabilizes the biradicaloid and prevents transannular through-space interaction resulting in the formation of a bicycle.

 Table 1:
 Selected bond lengths [Å] and angles [°] along with NAO partial charges [e] for 1Ter, 3Ter, 5Hyp, and 6Hyp.

	1Ter ^[a]	3 Ter ^[b]	5Hyp ^[c]	6 Нур
d(N–P)	1.720(2) ^[c]	1.716(1) ^[c]	1.585(2) ^[c]	1.734(3) ^[c]
d(PE) ^[b]	2.612(1)	2.6186(8)	2.53(6)	2.442(1)
≹ (NPN)	80.93 (8) ^[c]	80.56(8) ^[c]	106.9(1) ^[c]	83.5(1)
≮ (PNE) ^[b]	98.83(8)	99.44(6)	88.0(2)	89.5(1) ^[c]
≮ (NPNE) ^[b]	-5.4(1)	0.0	4.28(4)	27.8(1)
q(P)	+1.32	+0.83	1.29	-1.49
q(N)	-1.18	-1.03	-1.55	+1.16
$\Sigma q (NPNE)^{[b]}$	+0.28	-0.41	-1.22	-0.67

[a] Taken from reference [20]. [b] E = P for 1Ter, 3Ter, 6Hyp; E = Li for 5Hyp. [c] Averaged values are presented.

Computations of the electronic structure, and also MO and NAO analyses (NAO = natural atomic orbital)^[24b,c,30] support the assumption that 3Ter may be regarded as a biradicaloid with six delocalized π electrons (Figure 3).^[24c] NAO/MO analyses indicate an electron-rich 6π-electronic system with a p_{π} orbital occupation of 1.65 for the N (2 p_{π}) and 1.26 *e* for the P atoms $(3p_{\pi})$.^[24b,c] The overall charge of the P_2N_2 ring amounts to -0.41e (Table 1). Full optimization at the UB3LYP/6-31G(d,p) level of theory shows a singlet ground state with a planar N₂P₂ ring and no P…P bond. The singlet state of **3**Ter is 22.6 kcal mol⁻¹ lower in energy than the triplet state (UB3LYP/6-311 + G(d,p)//6-31G(d,p)).^[24b,c] UHF and CASSCF(2,2)/6-31G(d) calculations indicate open-shell character. The two dominant contributions to the CI wave function for the ¹A state are $\Phi({}^{1}A) = 0.93 |\pi_1^2 \pi_2^2 \pi_3^2 > -0.35|$ $\pi_1^2 \pi_2^2 \pi_4^2 > (\text{Figure 3 left, HOMO} = \pi_3, \text{LUMO} = \pi_4).^{[24c]}$ This corresponds to an occupation of the nonbonding π_3 orbital with 1.7 electrons and thus species 3 possesses considerably



Figure 3. Left: Representation of the π orbitals in 3 (c1, c2 = dominant contributions to the CI wavefunction). Right: Lewis representations of 3.

biradical character, in accord with computations on the $[ClC(\mu-PMes^*)]_2$ biradicaloid from Niecke et al.^[13] In the VB picture, compound 3 is best described by resonance between biradical structure (A) and dipole structures (B-E) as shown in Figure 3 (right). The calculated phosphorus and nitrogen NAO net charges are $q_{\rm P} = +0.83$ and $q_{\rm N} = -1.03e$, respectively, which would seem to support the conclusion that structures B-E are rather unlikely VB structures. However this conclusion ignores 1) the P–N σ bond polarization that occurs for the valence shell σ electrons: the total spd populations for these electrons are 2.91 (P) and 4.38e (N), respectively; and 2) the values of the valence-shell p_{π} AO populations, 1.26 (phosphorus $3p_{\pi}$) and 1.65 (nitrogen $2p_{\pi}$). Therefore the P–N σ -bond polarization rather than the π electron distribution is primarily responsible for the magnitudes of the atomic net charges.

Over the last decades only a very small number of planar four-membered ring molecules with an aromatic 6π -electronic structure have been isolated.^[12] Apart from the well-studied S₂N₂, which possesses 6% biradical character,^[12c,31] and its isoelectronic analogues P₄^{2-[32]} and S₄^{2+,[33]} only one anion of the type $[P(\mu-CR)]_2^{2-}$ has been reported.^[25] Biradicaloid **3** opens a new class with a N₂P₂ skeleton that can be derived from $[RC(\mu-P)]_2^{2-}$ by isoelectronic substitution of "C-" by N. Only recently, Roesky, Frenking et al. reported an almost planar but antiaromatic 4π -electron-containing stable dimeric silaisonitrile of the type $[Si(\mu-NTer)]_2$.^[27] It can be assumed that a two-electron-reduction process should yield another biradicaloid of the type $[Si(\mu-NTer)]_2^{2-}$, which would be isoelectronic to **3**Ter.

In summary, a high-temperature-stable biradicaloid $[P(\mu-NTer)]_2$ is presented for the first time. Biradicaloids **3**R (R = Ter, Hyp) are formed when mild reducing agents were employed and bulky substituents, such as R = Hyp and Ter, prevent dimerization. Furthermore, it was shown that biradicaloids **3**R can also be considered to be intermediates in the reactions of 1,3-dichloro-*cyclo*-diphosphadiazanes with stronger reducing agents, such as alkali metals, resulting in the formation of diazaphosphaallyl metal complexes. While the bulky Ter substituent does not allow addition of alkynes,

3Hyp forms alkyne-bridged species **6**Hyp upon addition of alkynes. Thus, highly reactive **3**Hyp prepared in situ can be used as a quenching reagent for further synthesis.

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