Insights into the Staudinger Reaction: Experimental and Theoretical Studies on the Stabilization of *cis*-Phosphazides

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Dedicated to Prof. Dr. Edgar Niecke on the occasion of his 60th birthday

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The Staudinger-model reaction H_3P (**1**) + HN_3 (**2**) → $H_3P=NH$ (**5**) + N_2 (**6**) has been investigated at the CCSD(T)/6-31G**//MP2(Full)/6-31G* level. Primary products formed in this reaction are the phosphazides $H_3P=N–N=NH$ (**3**) which exist as *trans* and *cis* isomers. In contrast to some previous assumptions, ***cis*-3** is 8.2 kcal mol^{-1} more stable than ***trans*-3** but decomposes rather easily into the expected products $H_3P=NH$ and N_2. This decomposition can be effectively hampered by intramolecular donor–acceptor interactions as shown by calculations on model compounds as well as by experiments. Thus the reaction of a methylene-σ^3,λ^3-phosphanyl-σ^5,λ^5-phosphorane with PhN_3 led to a new four-membered heterocycle containing a thermally remarkable stable *cis*-phosphazide moiety.

Since 1919 the reaction between azides and phosphanes (Staudinger reaction) has been widely used by phosphorus chemists for the preparation of λ^5-iminophosphoranes (phosphazenes).[1] In the course of the reaction the primary imination products, phosphazides, are formed, which are rarely stable under ambient conditions.[2] In a few cases, where R is strongly electron donating, R′ strongly electron withdrawing, or where both R and R′ are sterically bulky, remarkable stable phosphazides $R_3P=N-N=NR'$ have been isolated.[3][4] Here we wish to report on the first detailed ab initio study of the Staudinger reaction and a new possibility to stabilize phosphazides.

The Staudinger-model reaction H_3P (**1**) + HN_3 (**2**) → $H_3P=NH$ (**5**) + N_2 (**6**) has been investigated at the CCSD(T)/6-31G**//MP2(Full)/6-31G* level of theory.[5] In the first step of this reaction the *trans*-configured and *cis*-configured phosphazides ***trans*-3** and ***cis*-3** are formed, respectively. Subsequently, decomposition of these intermediates leads to the phosphazene **5** and dinitrogen (**6**) (Scheme 1).

In Figure 1, the geometry-optimized structures of the phosphazides ***trans*-3**, ***cis*-3**, the transition states **TS1**, **TS2**, and **TS3**, the phosphatriazete **4**, and the phosphazene **5** are shown. Calculated total energies of all species are given in Table 1 and atomic charges on P and N of ***trans*-3** and ***cis*-3** obtained by Natural Bond Orbital analyses (NBO) are given in Table 2.

The structures of some phosphazides have been determined experimentally.[3][4] Most of these compounds contain a *trans*-configured phosphazide moiety[3] while the *cis*-conformation[4] has rarely been observed. This led to the assumption that the *trans* conformers are more stable than their corresponding *cis* isomers. However, at least for the parent model system $H_3P=N-N=NH$ our calculations show a different picture: ***cis*-3** is more stable than ***trans*-3** by 8.2 kcal mol^{-1}. The isomerisation of ***trans*-3** to ***cis*-3** proceeds via the transition state **TS1** and requires an activation energy of 6.4 kcal mol^{-1}. Indeed, the *cis* isomer, though thermodynamically more stable, decomposes rather easily into $H_3P=NH$ (**5**) and N_2 (**6**). On the reaction coordinate, the transition state **TS2** has to be overcome, which is 8.2 kcal mol^{-1} higher in energy than ***cis*-3**. This reaction can be described as an intramolecular nucleophilic attack of the negatively charged nitrogen centre N3 (−0.55 e) on the positively charged phosphorus centre (+0.95 e). As a result, the P−N3 distance is shortened from 2.402 Å in ***cis*-3** to 1.880 Å in **TS2**. The approach of the N3 centre towards the phosphorus centre is accompanied by a pseudo-rotation at the phosphorus centre. Thereby, the formerly short P=N1 bond (1.673 Å in ***cis*-3**) is lengthened (1.924 Å in **TS2**) and the nitrogen centre N1 takes an axial position within the distorted trigonal-bipyramidal coordination sphere of the phosphorus centre.

The next product encountered on the reaction pathway is the C_1-symmetric λ^5-triazaphosphete **4**. This heterocycle is 6.7 kcal mol^{-1} higher in energy than ***cis*-3**. Molecule **4** is well-prepared for the cycloreversion leading towards the phosphazene **5** and dinitrogen. The P−N1 bond (1.951 Å) and N2−N3 bond (1.434 Å) are even longer than the ones in **TS2** while the N2−N3 bond is shorter. Calculations performed for **4** at higher levels of theory [MP4(Full) and

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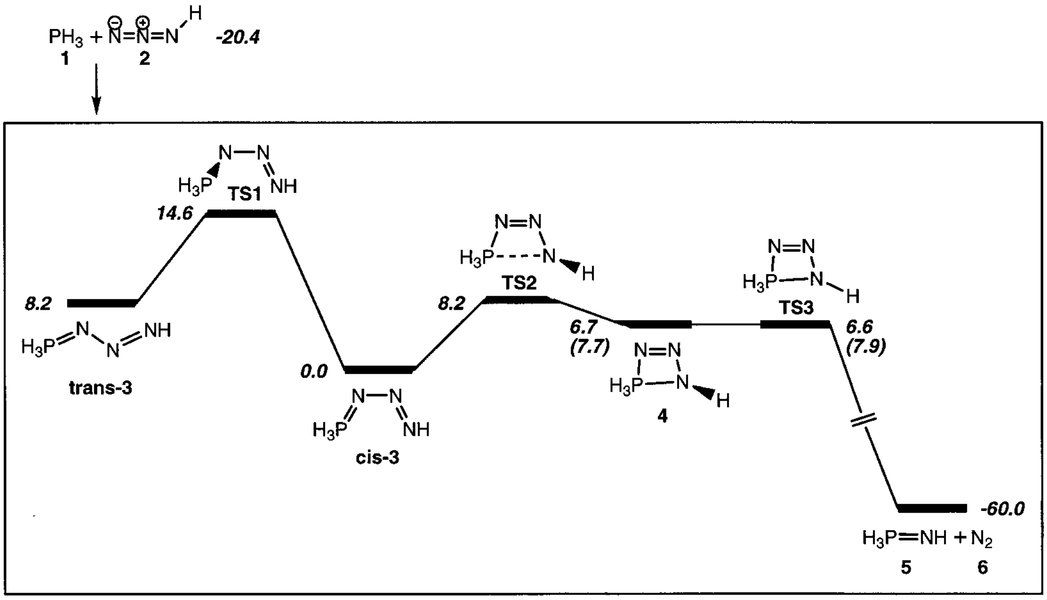
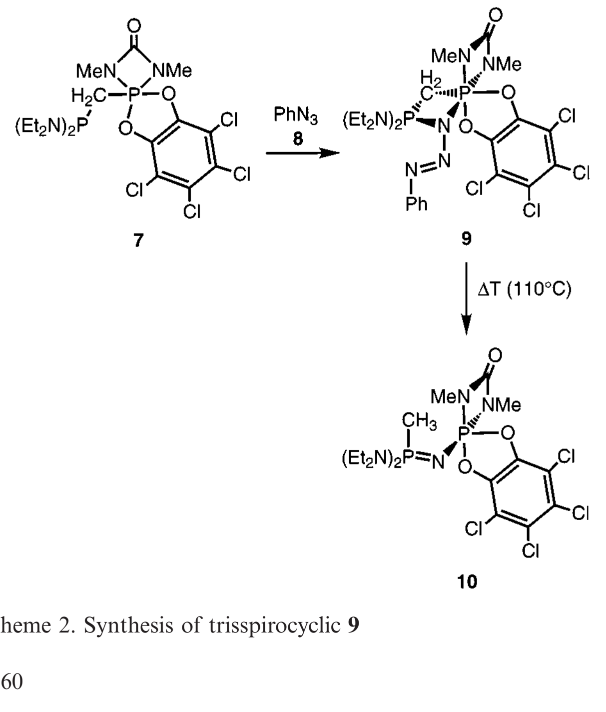


Scheme 1. Schematic representation of the isomerisation and decomposition pathways of ***cis*-3**; the refined and ZPE-corrected relative energies at the CCSD(T)/6-31G**//MP2(Full)/6-31G* level are given in kcal mol^{-1}; for **4** and **TS3** the refined relative energies at the CCSD(T) level without ZPE-correction are additionally given in parentheses

QCISD(Full)] confirm that triazete **4** is a local minimum on the energy hypersurface. However, without ZPE correction, **4** is only 0.2 kcal mol^{-1} lower in energy than **TS3**. Inclusion of zero-point energies reverses this ordering making **TS3** 0.1 kcal mol^{-1} lower in energy than **4**. This means that ordinary transition-state theory cannot be expected to describe this region of the hypersurface accurately. Therefore, we are not able to distinguish between a stepwise or concerted reaction mechanism at this point.[6] However, we can assume that ***cis*-3** decomposes via **TS2** to form phosphazene $H_3P{=}NH$ (**5**) with loss of dinitrogen.

During the decay of ***cis*-3** to **5** under extrusion of N_2 the valence configuration at N1 and N2 changes from sp^2 to sp. This process may be hampered when the lone pair at one of these nitrogen centres is involved in a donor–acceptor interaction. To test this idea we prepared the methylenephosphanyl phosphorane **7**[7] and reacted it with phenyl azide **8** (Scheme 2).



Scheme 2. Synthesis of trisspirocyclic **9**

The compound **7** contains a (λ^3,σ^3)-phosphorus centre, which can undergo a Staudinger reaction with an azide. To this phosphorus centre, a strongly positively charged (λ^5,σ^5)-phosphorus centre is bonded in the β position which can act as electron-pair acceptor. The reaction of **7** with **8** proceeds smoothly in diethyl ether without evolution of dinitrogen. The product **9** was recrystallized from toluene to afford colorless crystals suitable for an X-ray structure analysis. The result is shown in Figure 2, selected bond lengths and angles are given in the figure caption.

In compound **9** the azide moiety, indeed, takes a bridging position between the two phosphorus centres P1 and P2, thereby forming a planar four-membered ring. The P1–N1–N2–N3 unit shows a *cis* configuration. The P1–N3 distance (2.977 Å) is considerably longer than that calculated for ***cis*-3** (2.402 Å). However, apart from this distance, all other P–N and N–N bond lengths are in good agreement with distances and angles observed in ***cis*-3**. The intramolecular interaction between N1 and P2 augments the coordination number of P2 from five to six and the (λ^5,σ^6)-P2–N1 bond (1.812 Å) is, as expected, considerably longer than the P1=N1 bond (1.626 Å). The heterocycle **9** shows unusual thermal behavior when heated to 100–110°C in toluene. No dinitrogen evolution is observed but the iminophopshorane **10** is obtained which was unequivocally characterized by its NMR spectra. The mechanism leading to its formation is still unclear.

At this stage of our investigation, we returned to theoretical studies. Since the parent phosphazides ***trans*-3** and ***cis*-3**

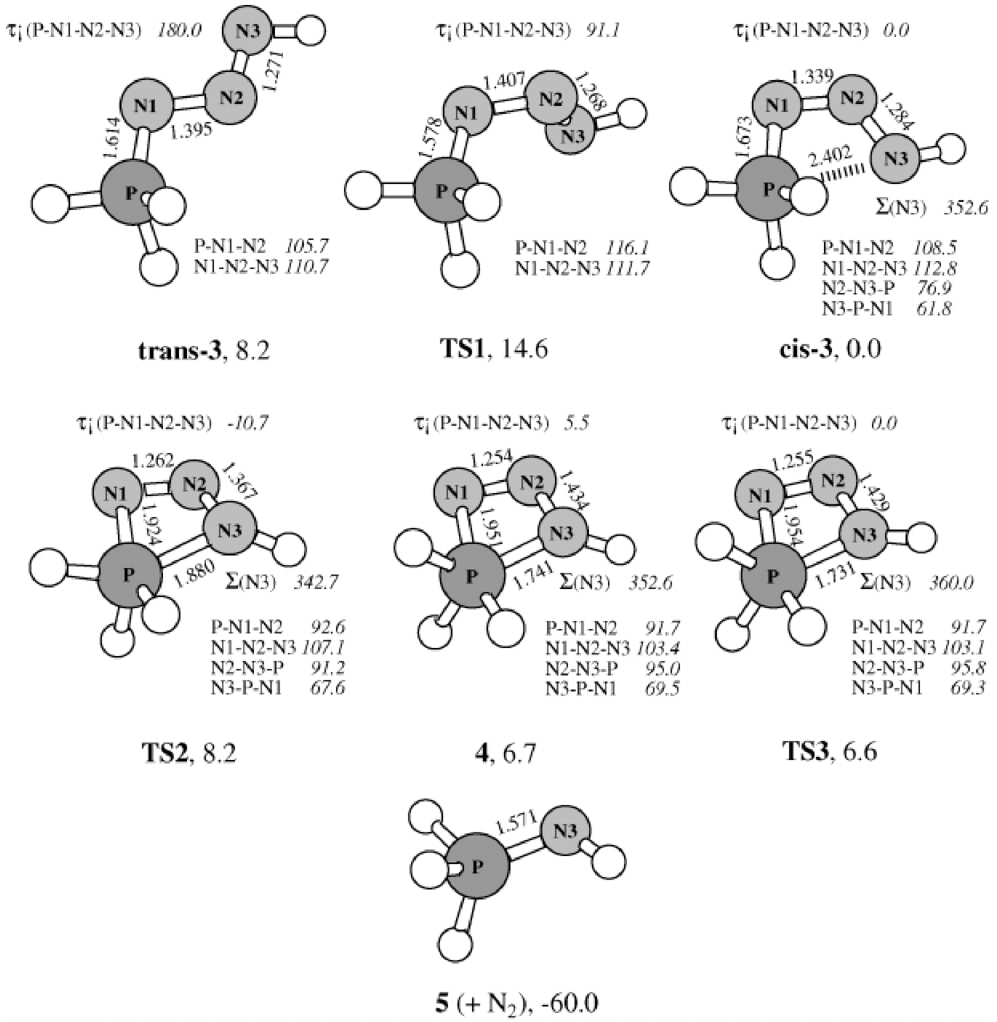


Figure 1. Schematic representation of the fully optimized MP2 structures of the Staudinger model reaction $H_3P + N_3H \rightarrow [H_3P{-}N{=}N{-}NH] \rightarrow H_3P{=}NH + N_2$ including selected bond lengths [Å], angles [°], and dihedrals τ [°]; relative energies are given in kcal mol^{-1}

Table 1. Energies for reactants, intermediates, transition states, and products of the reactions **1** + **2** → **3** → **5** + **6** and **12** → **13** → **15** + **6** as well as for the phosphazides ***cis*-11** and ***trans*-11**

	CCSD(T)/6-31G**//MP2(FULL)/6-31G*						
	sym	$E_{\mathrm{tot,opt}}$	$E_{\mathrm{tot,ref}}$	ZPE	N	$E_{\mathrm{rel,opt}}$	$E_{\mathrm{rel,ref}}$
1 + 2		–506.913507	–506.977975	29.2	[b]	–23.0	–20.4[c]
***cis*-3**	C_s	–506.884108	–506.952590	33.8	0	0.0	0.0
***trans*-3**	C_s	–506.869078	–506.938648	33.2	0	8.9	8.2
TS1	C_1	–506.858065	–506.928200	33.0	1	15.6	14.6
TS2	C_1	–506.870509	–506.937569	32.5	1	7.3	8.2
4	C_1	–506.872567	–506.940327	32.7	0	6.2	6.7[d]
TS3	C_s	–506.872441	–506.940001	32.5	1	6.0	6.6
5 + 6		–506.977098	–507.042359	30.1	[b]	–62.0	–60.0[c]
***cis*-11**	C_1	–1395.38109		78.7	0	0	
***trans*-11**	C_1	–1395.37594		78.8	0	3.3	
12	C_1	–571.393729	–571.503381	58.9	0	19.2	18.6
***cis*-13**	C_1	–571.427110	–571.535920	60.7	0	0.0	0.0
***trans*-13**	C_1	–571.418281	–571.527430	60.5	0	5.4	5.2
TS4	C_1	–571.391318	–571.499418	58.5	1	20.3	20.7
14	C_1	–571.497302	–571.600441	58.7	0	–46.0	–42.5
15 + 6		–571.524975	–571.611543	57.7	[b]	–64.3	–50.4[c]

[a] All structures were optimized at the MP2(Full)/6-31G* level ($E_{\mathrm{tot,opt}}$). Refined energies were obtained at the CCSD(T)/6-31G** level ($E_{\mathrm{tot,ref}}$), except for ***cis*-11** and ***trans*-11**, respectively. Total energies in Hartrees, zero point energies (ZPE, unscaled) and relative energies ($E_{\mathrm{rel,opt}}$, $E_{\mathrm{rel,ref}}$, ZPE correction included) in kcal mol^{-1}; N: number of negative frequencies. – [b] Frequency analyses show that **1** and **2**, **5** and **6** as well as **15** are local minima. – [c] No BSSE (basis-set superposition error) correction included. – [d] Calculations at higher levels of theory (MP4, QCISD) confirm that **4** is a local minimum on the hypersurface.

Table 2. Atomic charges of ***trans*-3** and ***cis*-3**

	atomic charges	
	***trans*-3**	***cis*-3**
P	1.090	0.953
N1	–0.830	–0.737
N2	–0.104	–0.002
N3	–0.383	–0.554

[a] Selected atomic charges for the phosphazides ***trans*-3** and ***cis*-3**, respectively, obtained by NBO analysis at the MP2(Full)/6-31G* level.

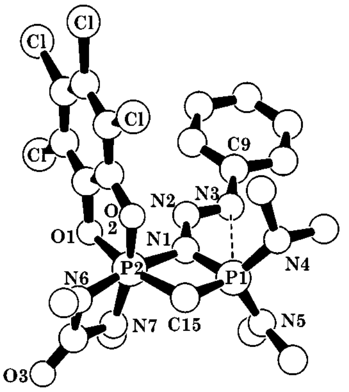


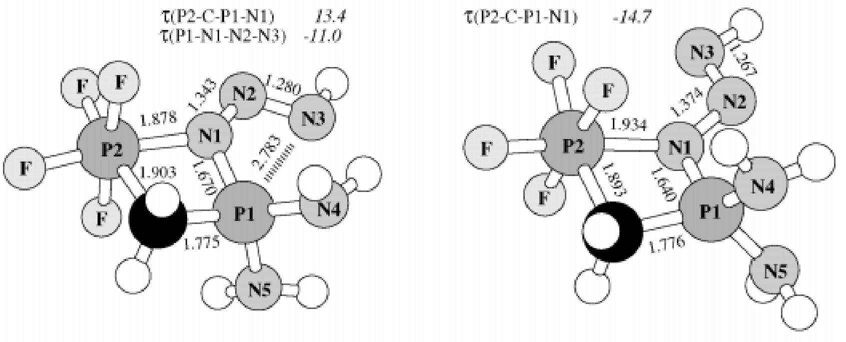
Figure 2. X-ray structure of **9** including selected bond lengths [Å] and angles [°]; H atoms and disordered ethyl groups at N4 and N5 are omitted for clarity: P1−N1 1.626(6), P1−N4 1.622(5), P1−N5 1.612(5), P1−C15 1.770(6), P1−N3 2.928(5), P2−N1 1.812(5), P2−N6 1.754(5), P2−N7 1.761(5), P2−C15 1.865(6), P2−O1 1.758(4), P2−O2 1.754(5), N1−N2 1.361(6), N2−N3 1.254(6); N1−P1−C15 84.0(3), N4−P1−N5 108.0(3), N1−P2−C15 76.4(2), O1−P2−O2 89.1(2), N6−P2−N7 72.9(3), P1−C15−P2 96.0(3), P1−N1−P2 103.4(3), P1−N1−N2 129.3(4), P2−N1−N2 126.9(4), N1−N2−N3 115.1(6), N2−N3−C9 117.8(6)

are rather different from the experimentally obtained structure **9**, we have performed ab initio calculations for ***cis*-11** and ***trans*-11** which are better models. The PF_4 moiety was chosen as substitute for the acceptor group including the hexa-coordinated P2 centre in **9** and the $P(NH_2)_2$ group was chosen to replace the $P1(NEt_2)_2$ unit. The structures of ***cis*-11** and ***trans*-11** were also optimized at the MP2(Full)//6-31G* level and are shown in Figure 3.

The *cis* isomer is again more stable than the *trans* isomer. However, at the MP2(Full)/6-31G* level, the energy difference amounts to only 3.3 kcal mol^{-1} and is 5.6 kcal mol^{-1} smaller than that observed for the parent compounds ***cis*-3** and ***trans*-3**. Thus, the observed *cis*-configuration of the P−N1−N2−N3 unit in **9** might be simply preferred for steric reasons. Generally, the agreement between the calculated structure of ***cis*-11** and that of **9** is acceptable. The four-membered heterocycle which is planar in **9** deviates slightly from planarity in ***cis*-11** and, in an opposite sense, in ***trans*-11**. As was also observed experimentally, the P2−N1 and P2−C bonds pointing away from the hexa-coordinated phosphorus centre P2 are considerably longer than corresponding P1−N1 and P1−C bond lengths. The largest deviation is seen in the intramolecular P1−N3 contact, which is about 0.2 Å longer in ***cis*-11** than the experimental value observed in **9**.

Since the theoretical investigation of the decomposition pathways of **11** is very expensive, we investigated the boromethyl phosphazides **12** and **13**. The decomposition of these compounds is easier to study at the level of theory used throughout this paper and **12** and **13** should serve as reliable models for the study of the effect of intramolecular donor−acceptor interactions. The structures optimized at the MP2(Full)/6-31G* level are shown in Figure 4 including selected bond lengths and angles.

Rotation around the P−C bond interconverts **12** to ***cis*-13**. Intramolecular nucleophilic attack of N1 onto the boron centre leads to the formation of the four-membered B,C,P,N heterocycle. The energy gained by this process amounts to 18.6 kcal mol^{-1} and can be taken as measure of the donor-acceptor stabilization energy of the N1−B interaction. The heterocycle ***cis*-13** is 5.2 kcal mol^{-1} more stable than ***trans*-13**. However, this energy difference is again smaller than that found for the parent compounds ***cis*-3** and ***trans*-3**, respectively (8.2 kcal mol^{-1}). Obviously, the *trans*-isomers become *thermodynamically* more stabilized than the *cis*-isomers by intramolecular donor-acceptor interactions. The latter remain, however, energetically favored. The structure of the *cis*-configured phosphazide moiety P1−N1−N2−N3 does not differ significantly from the one calculated for ***cis*-11** or the one observed in **9**. Note that the P−N3 contact becomes considerably longer (ca. 0.3 Å) in the cyclic compound ***cis*-13** (2.767 Å) while in the acyclic



cis-11

trans-11, 3.3

Figure 3. Schematic representation of the isomers ***cis*-11** and ***trans*-11** including bond lengths [Å] and dihedrals τ [°]; the relative energy is given in kcal mol^{-1}

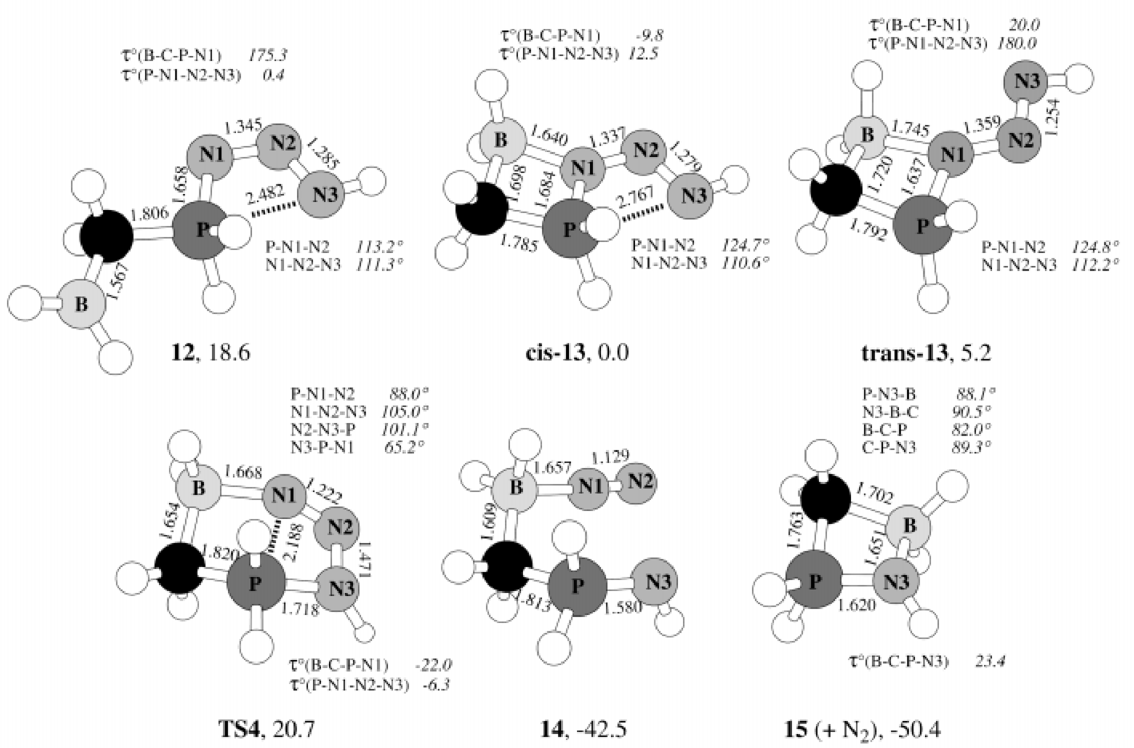


Figure 4. Schematic representation of the fully optimized MP2 structures of the (boromethyl)phosphazides $(H_2BCH_2)H_2P{=}N1{-}N2{=}N_3H$ including selected bond lengths [Å], angles [°], and dihedrals τ [°]; relative energies are given in kcal mol^{-1}

structure **12** this distance (2.482 Å) lies in the same range as has been calculated for the parent compound ***cis*-3** (2.402 Å). The cleavage of dinitrogen from ***cis*-13** proceeds via the bicyclic transition state **TS4** which is 20.7 kcal mol^{-1} higher in energy. This activation barrier is 12.5 kcal mol^{-1} higher than that calculated for the decay of ***cis*-3**. The phosphazene **14** is formed exothermically (−42.5 kcal mol^{-1}) and still contains the dinitrogen N_2 molecule coordinated to the Lewis-acidic boron centre. After dissociation of N_2, the heterocycle **15** is observed as the final product and encloses the thermodynamically highly favored reaction sequence. This example shows that intramolecular donor−acceptor interaction between an electron pair acceptor and the lone pair at the N1 centre may efficiently hamper *kinetically* the decay of *cis*-phosphazides into phosphazenes and dinitrogen.

Experimental Section

Calculations: The calculations were performed with the GAUSSIAN 94 program package.[8] All structures were fully optimized at the MP2(Full) level using the polarized split-valence-shell 6-31G* basis set.[5a,5b] Refined energies were obtained at the CCSD(T) level,[5c−5e] except for ***cis*-11** and ***trans*-11**, in conjunction with the slightly extended basis set 6-31G**,[5b] which also contains p polarization functions on the hydrogen atoms. The vibrational frequency calculations were carried out to characterize all structures as minima or transition states. Relative energies were corrected for zero-point vibrational energy (ZPE) using the unscaled MP2 corrections. Atomic charges were obtained at the MP2(Full)/6-31G* level according to Reed and Weinhold's NBO analysis,[9] which is implemented in GAUSSIAN 94. Selected total and relative energies of all calculated structures are presented in Table 1.

***cis*-Phosphazide 9**: A solution of **7**[7] (150 mg, 0.27 mmol) in 2 mL of diethyl ether was treated with 50 mg (0.42 mmol) of phenylazide and the reaction mixture was allowed to stay at room temperature for 30 min. The bottom of the flask was rubbed by a glass stick to promote the crystallization and after formation of the first crystals the solution was allowed to stay at −18 °C for 12 h. Crystals of **9** were separated and recrystallized from toluene. M.p.: 139−141 °C. Yield 116 mg (64%). − ^1H NMR (90 MHz, $CDCl_3$): 1.12 [t, $^3J(H,H)$ = 7.02 Hz, 12 H, NCH_2CH_3], 2.77 [d, $^3J(P,H)$ = 14.4 Hz, 6 H, NCH_3], 2.9−3.4 (m, 8 H, NCH_2CH_3), 2.9−3.4 (m, 2 H, PCH_2P), 7.23−7.52 (m, 5 H, C_6H_5). − ^{13}C NMR (22.5 MHz, $CDCl_3$): 13.2 [d, $^3J(P,C)$ = 2.9 Hz, 4C, Et], 27.9 [d, $^2J(P,C)$ = 4.9 Hz, 2C, NMe], 38.6 [dd, $^1J(P,C)$ = 86.8 Hz, $^1J(P,C)$ = 122.9 Hz, P−C−P], 39.4 [d, $^2J(P,C)$ = 5.9 Hz, 4C, Et], 113.6 [d, $^2J(P,C)$ = 16.5 Hz, 2C, Ar], 121.4 (s, 2C, Ar), 121.8 (s, 2C, Ar), 129.1 (s, 1C, Ar), 129.21 (s, 2C, Ar), 143.2 (s, 1C, Ar), 148.2 (s, 2C, Ar), 160.9 [d, $^2J(P,C)$ = 12.6 Hz, CO]. − $C_{24}H_{33}Cl_4N_7O_3P_2$: calcd. C 42.94, H 4.95, N 14.60; found C 42.47, H 4.98, N 14.82.

Iminophosphorane 10: ^{31}P NMR (C_6D_6): 23.5 [d, $^2J(P,P)$ = 44 Hz]; −52.1 [d, $^2J(P,P)$ = 44 Hz]. − ^1H NMR (C_6D_6): δ = 0.66 [t, $^3J(H,H)$ = 7.08 Hz, 12 H, Et], 1.09 [d, $^2J(P,H)$ = 14.2 Hz, $P{-}CH_3$], 2.3−2.7 (m, 8 H, Et), 2.87 [d, $^3J(P,H)$ = 13.4 Hz, NCH_3].

X-ray Analysis of *cis*-Phosphazide 9: Orthorhombic, space group *Pbca*; a = 18.284(14), b = 17.158(12), c = 20.37(2) Å; V = 6392(8) $Å^3$; Z = 8, MoK_α-radiation, $2\Theta_{max}$ = 41.4°. 3011 independent reflections; direct methods; full-matrix least-squares refinement based on F^2 with SHELXTL (Version 5.0); R_1 = 4.6%, wR_2 = 9.32% (based on F^2) for 389 parameters and 3010 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101754. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) +44-1223/336033; E-mail: deposit@chemcrys.cam.ac.uk].

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