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On the Staudinger Reaction of $SP(N_3)_3$ with PPh_3 and $(Me_3Si)_2N–(Me_3Si)N–PPh_2$

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The Staudinger reactions of $SP(N_3)_3$ (**1**) with 1, 2 and 3 equiv. of triphenylphosphane PPh_3 and $(TMS)_2N–(TMS)N–PPh_2$ (**2**) have been investigated (TMS = Me_3Si). Reaction with PPh_3 yields the single and double Staudinger products $SP(N_3)_2NPPh_3$ (**3**) and $SP(N_3)(NPPh_3)_2$ (**4**), but not the triple, while the reaction with **2** results only in the formation of the single Staudinger product $SP(N_3)_2NPPh_2[N(TMS)N(TMS)]_2$ (**5**). Compound **5** is air- and moisture-sensitive but stable under argon over a long period in the solid state and in common organic solvents. Although there are covalently bound azide groups in **3**, **4** and **5**, these Staudinger products are neither shock- nor heat-sensitive in contrast to **1**. Furthermore **3**, **4** and **5** are easily prepared in bulk (yield > 95 %), and unlimitedly stable when cooled and stored in the dark. Compound **5** is thermally stable up to over 150 °C while **3** and **4** are stable only up to 96 °C. However, when a solution of **5** is heated, a new surprising eight-membered ring (**6**) is formed in an intermolecular $TMS–N_3$ elimination reaction. The structure and bonding is discussed on the basis of experimental X-ray data and theoretical B3LYP calculations (thermodynamics, energy landscape and charge distribution).

Introduction

As early as 1919, Staudinger and Meyer investigated the reaction of triphenylphosphane and phenylazide in diethyl ether.[1] Ever since, this reaction has been known as the Staudinger reaction and describes an oxidation of phosphorus(III) to phosphorus(V) compounds, which is accompanied by a linkage of a P (phosphane) and a N (azide) atom of two different molecules upon N_2 release. With respect to the azide and phosphorus(III) compounds, the Staudinger reaction is very flexible. Hence, a great diversity of iminophosphanes and their applications are well known.[2–6] Phosphorus(V) nitrogen species represent a well-established group of compounds that is still growing. Of special interest are PN compounds that can be used as interesting reagents in organic synthesis.[7]

Recently, we reported on the reaction of 2,4,6-triazido-1,3,5-triazine with triphenylphosphane resulting in the formation of different triphenylphosphanimino-azido- or tetrazolo[1,3,5]triazines, depending on the stoichiometry of the azide and phosphane component (1:1, 1:2, 1:3).[8] Because the azido group in 2,4,6-triazido-1,3,5-triazine is attached to a C atom adjacent to an annular nitrogen, it can spontaneously cyclise to give a tetrazole.

Lately, the chemistry of hydrazinophosphanes of the type $(TMS)_2N–(TMS)N–PR_2$ (R = Ph, Cl; TMS = Me_3Si) has attracted considerable interest.[9] Experimentally and theoretically the intramolecular $GaCl_3$-assisted TMS–Cl elimination in $(TMS)_2N–N(TMS)–PCl_2$ has been studied, resulting in the first binary triazadiphosphole.[10]

We found it of interest to investigate the Staudinger reaction of hydrazinophosphanes with phosphorus azides. Table 1 displays a compilation of neutral phosphorus azides. However, only a few neutral singly, doubly or multiply substituted phosphorus azides are known that have been structurally characterised (Table 1). More structural data of phosphorus azides are needed to gain further insight into the relationship between bonding and stability.

In this study we demonstrate that the final products of the reaction of highly explosive $SP(N_3)_3$ (**1**) with PPh_3 and *N,N′,N′*-[tris(trimethyl)silyl]hydrazinodiphenylphosphane $[(TMS)_2N–(TMS)N–PPh_2]$ (**2**), as well as their distribution, strongly depend on the reaction conditions, stoichiometry and temperature (Figure 1). Depending on the temperature, different products are formed, which can be isolated and characterised.

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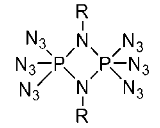
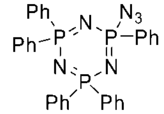
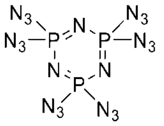
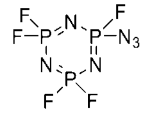
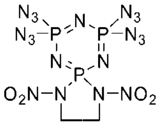
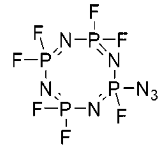
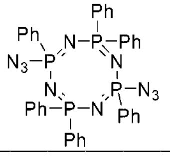
Table 1. Hitherto known neutral phosphorus azides.

Species	Reference
$P(N_3)_3$	[29,30,31]
$P(N_3)_5$	[29]
$PCl_{5-n}(N_3)_nL$ (n = 0–4) L = pyridine	[32]
$OP(N_3)_3$	[29,30]
$SP(N_3)_3$	[30]
$SPX_n(N_3)_{3-n}$ (X = Cl, Br; n = 1,2)	[30]
$SPX_n(N_3)_{3-n}$ (X = Cl, Br; n = 1,2)	[30]
$RP(N_3)_2$, R = Mes* [a]	[24,33]
$R_2P(N_3)$, R = *e.g.* N*i*Pr$_2$,[a] CF_3, F	[24,24g,34,35,36][a]
$OPR_2(N_3)$, R = H, NMe_2, NH*i*Pr, *O*-bis[4-(phenylazo)phenyl] ester, OCH_2CF_3,	[37,38,39]
$SPR_2(N_3)$, R = Me[a]	[24a,40]
	$R = C_6H_5$,[a] C_6F_5[a] [41,42]
	[43]
	[44]
	[45a,b]
	[46]
	[44b]
	[47]

[a] Characterised by X-ray analysis.

Results and Discussion

Reaction of $SP(N_3)_3$ with PPh_3

By addition of 1 equiv. of triphenylphosphane to a solution of **1** in ether at ambient temperature, initially a yellow-green intermediate is formed, thought to be due to the formation of $R–NNN–P(C_6H_5)_3$ [R = $SP(N_3)_2$]. This adduct has only a fleeting existence and decomposes by giving off N_2, resulting in the formation of a monophosphaniminodiazide species, $SP(N_3)_2(NPPh_3)$ (**3**) (Figure 1), as illustrated by ^{31}P NMR experiments; two duplets with the same intensity are detected at δ = 50.3 ppm [$S\mathit{P}(N_3)_2NPPh_3$] and 16.8 ppm [$SP(N_3)_2N\mathit{P}Ph_3$] ($^2J_{PP}$ = 22.6 Hz). By addition of a second equiv. of triphenylphosphane, again N_2 release was observed. ^{31}P NMR spectroscopic data suggest the exclusive formation of only one species (Table 2): a triplet at δ = 42.4 ppm [t, $S\mathit{P}(N_3)(NPPh_3)_2$] and a duplet at 7.5 ppm [d, $SP(N_3)(N\mathit{P}Ph_3)_2$] are observed as expected for the double Staudinger product, $SP(N_3)(NPPh_3)_2$ (**4**) ($^2J_{PP}$ = 7.6 Hz). Addition of a third equiv. of PPh_3 results in no further reaction, as shown by ^{31}P NMR experiments. Also heating under reflux condition of this reaction mixture does not support the release of a third molecule N_2 and finally the formation of the triple Staudinger product [$SP(NPPh_3)_3$, Figure 1].

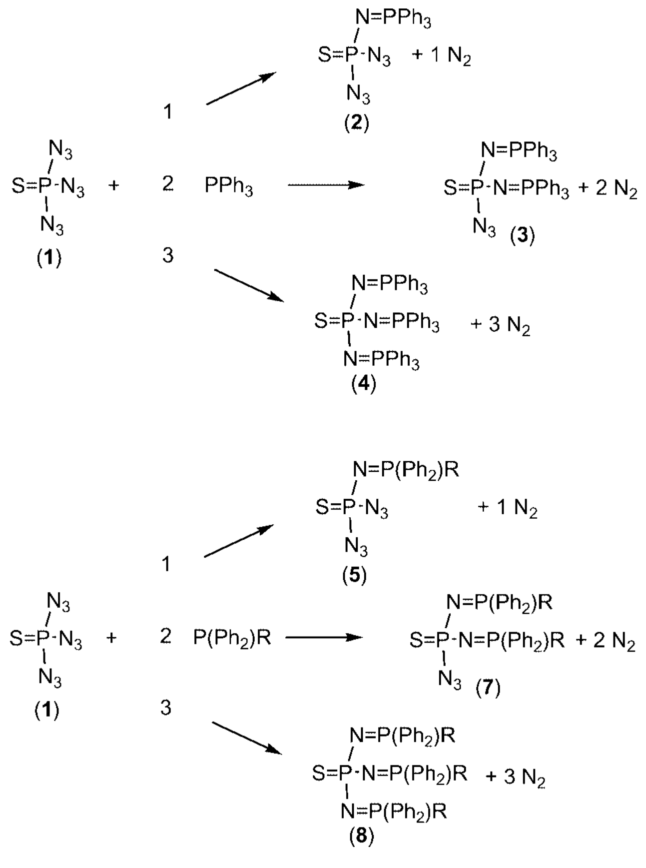


Figure 1. Top: Staudinger reaction of thiophosphoryl azide, $SP(N_3)_3$, with triphenylphosphane; bottom: Staudinger reaction of thiophosphoryl azide and *N*,*N*′,*N*′-[tris(trimethyl)silyl]hydrazinodiphenylphosphane, $(TMS)_2N–(TMS)N–PPh_2$ (**2**) [R = $N(TMS)–N(TMS)_2$].

Table 2. ^{31}P NMR spectroscopic data of different Staudinger products and the starting materials.

Compound	δ [ppm]	$^2J_{PP}$ [Hz]
$SP(N_3)_3$ (**1**)	65.0 (s), ref.[29]	–
$(Me_3Si)_2N–(Me_3Si)N–PPh_2$ (**2**)	61.4 (s), ref.[9]	–
$SP(N_3)_2NPPh_3$ (**3**)	50.3 (d); 16.8 (d)	22.6
$SP(N_3)(NPPh_3)_2$ (**4**)	42.4 (t); 7.5 (d)	7.6
$SP(N_3)_2NPPh_2N(TMS)N(TMS)_2$ (**5**)	46.6 (d); 26.5 (d)[a]	34.3

[a] ^{31}P MAS: 30.7 and 51.0 ppm.

Reaction of $SP(N_3)_3$ with $Ph_2P–N(TMS)N(TMS)_2$ (TMS = Me_3Si)

Similar to the reaction with PPh_3, 1 equiv. of $Ph_2P–N(TMS)N(TMS)_2$ reacts spontaneously with $SP(N_3)_3$ in an ether/acetonitrile mixture at ambient temperature to give the single Staudinger product $SP(N_3)_2NPPh_2[N(TMS)-N(TMS)]_2$ (**5**). As expected, two duplets, at δ = 46.6 ppm $\{SP(N_3)_2N–PPh_2[N(TMS)N(TMS)_2]\}$ and 26.5 ppm $\{SP(N_3)_2NPPh_2[N(TMS)N(TMS)_2]\}$ ($^2J_{PP}$ = 34.3 Hz), are observed in the ^{31}P NMR experiment (^{31}P MAS: 30.7 and 51.0 ppm). The presence of two remaining azide groups in the single Staudinger product (Figure 1) was also deduced from Raman and IR spectroscopy. Bands at 2153 and 2129 cm^{-1} assigned to the characteristic asymmetric stretching vibration of the azide group in combination with the molecular peak (mass spectrometry) supported this assumption. Crystals (colourless plates) of sufficient quality for X-ray structure determination were obtained from a colourless ether/CH_3CN solution of **5** after stepwise removal of solvent at –10 °C.

In contrast to the Staudinger reaction with PPh_3, addition of another equivalent of **2** to **5** leads to no further substitution in solution, even upon long heating.[11] However, when this reaction mixture was slowly cooled, two different types of crystals were obtained within two weeks: colourless plates and needles. X-ray investigations of crystals of both types revealed a surprising eight-membered ring, **6**, for the colourless needles and again the single Staudinger product **5** for the plates.

The exothermic formation ($\Delta_{calc}E$ = –8.8 kcal/mol, see computational details) of an eight-membered P_4N_4 ring starting from **5** seems to be quite interesting, as two intermolecular TMS–N_3 elimination steps (corresponding to two condensation steps) are required (Figure 2).

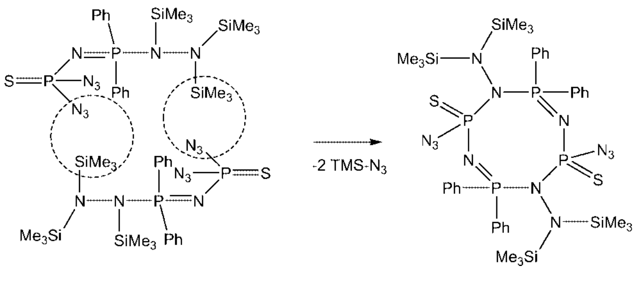


Figure 2. Formation of **6** by two intermolecular TMS–N_3 elimination steps (TMS = Me_3Si).

The single Staudinger product **5** is air- and moisture-sensitive but stable under argon over a long period in the solid state and in common organic solvents (e.g. benzene, CH_2Cl_2, diethyl ether etc.). Although there are two azide groups, **5** is neither shock- nor heat-sensitive, is easily prepared in bulk (yield > 95%) and infinitely stable when stored in a sealed tube and kept cool at 5 °C in the dark. Compound **5** is thermally stable up to over 150 °C while **3** and **4** are stable only up to 96 °C. At these temperatures decomposition starts, accompanied by a slow release of nitrogen (MS experiments).

X-ray Structure Elucidation of 5 and Bonding

Compound **5** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The perspective view of **5** is depicted in Figure 3 and selected bond lengths and angles are given in Table 3.

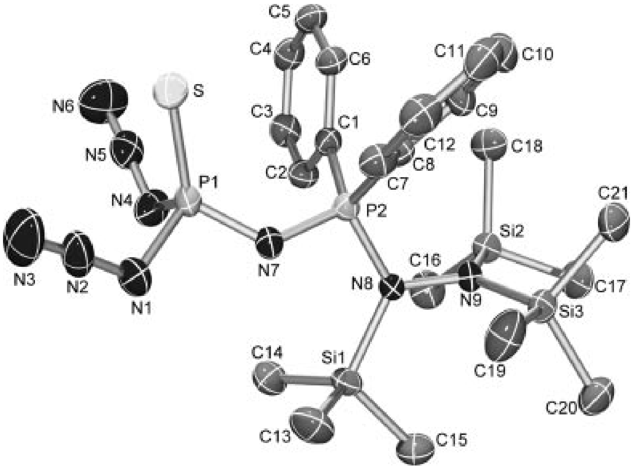


Figure 3. ORTEP drawing of the molecular structure of **5** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity).

Table 3. X-ray analysis of **5**: selected bond lengths [Å] and angles [°].

S–P1	1.9305(8)	Si1–N8	1.803(2)
P1–N1	1.713(3)	Si2–N9	1.767(2)
P1–N4	1.713(3)	Si3–N9	1.776(2)
P1–N7	1.583(2)	N1–N2	1.235(4)
P2–N7	1.586(2)	N2–N3	1.135(4)
P2–N8	1.662(2)	N4–N5	1.225(3)
P2–C1	1.801(2)	N5–N6	1.124(4)
P2–C7	1.795(2)	N8–N9	1.475(3)
S–P1–N1	113.00(9)	P1–N1–N2	116.3(2)
S–P1–N4	111.91(8)	N1–N2–N3	175.2(3)
S–P1–N7	123.55(8)	P1–N4–N5	118.5(2)
N1–P1–N4	99.3(1)	N4–N5–N6	174.0(3)
N1–P1–N7	99.9(1)	P1–N7–P2	129.1(1)
N4–P1–N7	105.9(1)	P2–C1–C2	117.5(2)
N7–P2–N8	103.2(1)	P2–C1–C6	123.2(2)

Both P^V atoms in **5** sit in a slightly distorted tetrahedral environment (angles around the P atoms between 99 and 112°) with the two azide groups at P1 in a *cis* position to the sulfur atom. Interestingly, two further isomers are possible with respect to the two azide groups: (i) only one azide group in a *trans* position, and (ii) both azide groups in a *trans* position to the sulfur atom. In agreement with the experiment, the close inspection of the conformational space of **5** revealed the experimentally observed *cis/cis* isomer to be the global minimum. The potential energy surface (PES) with respect to the rotation about all P–N bonds is very flat (see Supporting Information). The energy difference between the rotamers is smaller than 8 kcal/mol. The largest energy gap was found for the *cis/trans* isomers, whereas a *trans/trans* arrangement of both azide groups does not represent a minimum on the PES of **5**.

As shown on numerous occasions,[12] both covalently bound azide groups display a *trans*-bent configuration (regarding the P atom) with a N–N–N bond angle of 175.2(3) (N1–N2–N3) and 174.0(3)° (N4–N5–N6). The P1–N7–P2 angle is rather large at 129.1(1)° compared to the N9–N8–P2 angle at 117.4°(1). Another interesting feature of this structure is the almost planar environment of both hydrazine nitrogen atoms (<Si3–N9–Si2–N8 = 173.1, <N9–N8–Si1–P2 = 177.1°; all N–N–X angles are between 117 and 121°, X = P, Si; Table 3), however both planes are almost perpendicular to each other. Hence, as displayed by NBO analysis,[13] the lone pair on both nitrogen atoms is localised in a pure p-type atomic orbital. Both lone pairs are also perpendicular to each other.[9]

Three different types of P–N bond lengths are found: (i) the longest between P1 and the N atoms of the azide groups with 1.713(3) Å, (ii) 1.662(1) Å for the P2–N8 bond (N atom of the hydrazine group) and (iii) the smallest with 1.583(2) and 1.586(2) Å for the two P–N bonds of the dicoordinated imino N atom connecting the two P atoms. These P–N distances are substantially shorter than the sum of the covalent radii [$d_{cov}(N–P) = 1.8$, $d_{cov}(N{=}P) = 1.6$ Å],[14,15] which indicates partial double bond character, especially for the P1–N7 and P2–N7 bonds. A typical P–N bond with π character is found in R–P=N–R′ species with P–N distances between 1.495(4) Å (R = Cl, R′ = aryl)[16] and 1.619(2) Å [R = *t*Bu$_2$P, R′ = N(SiMe$_3$)$_2$].[17] According to NBO analysis, all P–N bonds are highly polarised (25–27% P, 73–75% N) and almost ideally covalent between the adjacent N–N and P–S bonds (P: 48%, S: 52%).

Figure 4 shows the energetically preferred Lewis representation (from NBO analysis) along with the calculated partial charges of **5**, indicating a highly ionic molecular system.[18] Both four-coordinate P atoms formally obey the octet rule by forming only four single bonds. A positive formal charge is found on both P atoms and a negative on the dicoordinated N atom and the S atom. The experimentally found short P–N (between P1–N7 and P2–N7, Table 3) and P–S bonds possess double bond character, which can be explained by intramolecular donor–acceptor interactions (hyperconjugation, noncovalent effects) along the P1(S)–N7–P2 moiety (Figure 3). As shown by NBO analysis (see below), these interactions describe a highly delocalised π system including the lone pairs of the dicoordinated N atom (N7) and the S atom but *not* the tricoordinated N atom (N8).[19]

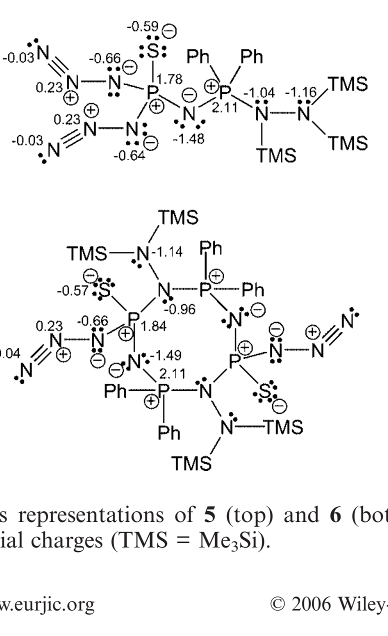


Figure 4. Lewis representations of **5** (top) and **6** (bottom) along with NPA partial charges (TMS = Me$_3$Si).

X-ray Structure Elucidation of 6 and Bonding

$SP(N_3)[NP(Ph)_2NN(TMS)_2]_2$ (**6**) crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Figure 5, Table 4). The eight-membered P_4N_4 ring adopts a chair conformation with all four N atoms being in one plane as well as all four P atoms. An inversion centre is found right in the middle of the P_4N_4 ring. Interestingly, all N and P ring atoms of each of the monomeric fragments lie within a plane (e.g. N1–P1–N2–P2 = 3.6°). These two N–P–N–P planes are distorted by about 104°, forming the eight-membered P_4N_4 chair. As two tri- and dicoordinated nitrogen atoms form the P_4N_4 ring, **6** cannot be regarded to be a phosphazene, but a tetrazatetraphosphocine with two formal double and two single P–N bonds. Traditional bonding descriptions for cyclic PN rings have involved N(2p)–P(3d) overlap,[20] both in and perpendicular to the plane of the PN ring. However, this model is not consistent with the fact that phosphorus makes little or no use of its 3d orbitals (see above).[18,21] In accord with this, NBO analysis localises only single bonds (Figure 4) within the ring, again obeying the octet rule for all involved elements. However, according to the X-ray analysis, two smaller P–N bond lengths [π PN: d(N1–P2) = 1.573(3), d(N1–P2) = 1.586(3) Å] and two longer P–N distances [σ PN: d(N2–P1) = 1.703(2), d(N2–P2) = 1.707(2) Å] are experimentally observed. Both types of P–N bond lengths are a little bit shorter than the sum of the covalent radii for a single [$d_{cov}(N–P) = 1.8$ Å] and a double bond [$d_{cov}(N{=}P) = 1.6$ Å],[22,23] indicating a certain degree of multiple bond

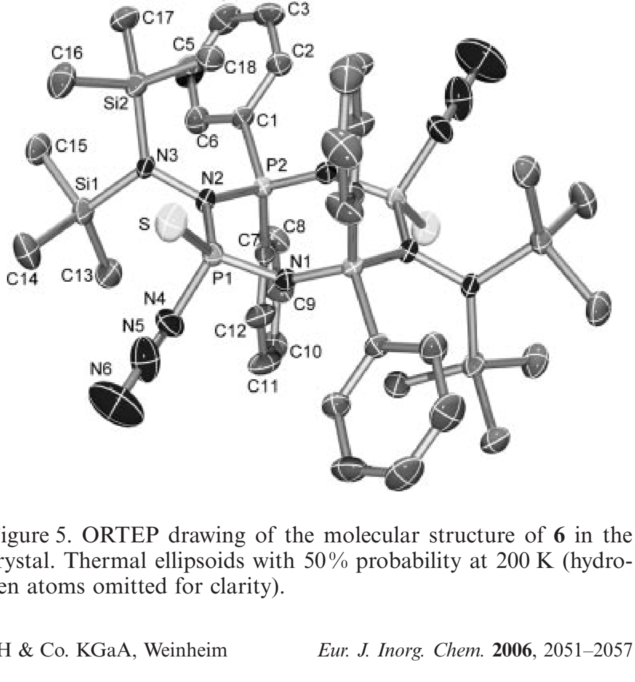


Figure 5. ORTEP drawing of the molecular structure of **6** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity).

character due to intramolecular donor–acceptor interactions. For comparison, the P–NNN distance with 1.738(3) Å represents a typical single bond.

Table 4. X-ray analysis of **6**: selected bond lengths [Å] and angles [°].

S–P1	1.932(1)	P2–C1	1.805(3)
P1–N1	1.586(3)	P2–C7	1.810(3)
P1–N2	1.703(2)	N2–N3	1.462(3)
P1–N4	1.738(3)	N2–P2	1.707(2)
P2–N1	1.573(3)	N4–N5	1.113(5)
P2–N2	1.707(2)	N5–N6	1.193(7)
N1–P1–N2	104.9(1)	N1–P2–N2	108.9(1)
N1–P1–N4	103.1(1)	N1–P2–C1	108.5(1)
N2–P1–N4	99.6(1)	N2–P2–C1	108.4(1)
N1–P1–S	122.1(1)	N1–P2–C7	114.8(1)
N2–P1–S	115.35(9)	N2–P2–C7	110.3(1)
N4–P1–S	108.9(1)	C1–P2–C7	105.6(1)

NBO analysis of **6** gives an almost identical picture compared to **5** (Figure 4) with respect to the type and magnitude of intramolecular donor–acceptor interactions, charge distribution and bond properties. Upon ring closure the partial charges of all atoms hardly change. The same holds for polarisation effects (similar PN and SP bond polarisation, see above) and the intramolecular donor–acceptor interactions describing the π system along the P–N moieties.[19,20] Only a close inspection of these interactions utilising the NBO partitioning scheme clearly indicates a highly delocalised π system along the P1(S)–N1–P2 moiety, which includes the lone pairs of both the S and the dicoordinated N atoms but not the azide group and the tricoordinated N atoms. These noncovalent effects represent typical $n(X) \rightarrow \sigma^*(Y–Z)$ hyperconjugative interactions (n = sp^λ- or p-type lone pair; X = S, N1; Y = P1, P2; Z = C1, C7, S, N1, N2, N4) and explain the partial double bond character of the P1–S, P1–N1 and N1–P2 bonds (Figure 4 and Figure 5).[19,20]

To summarise, the molecular and electronic structure of **6** strongly resembles the molecular structure of **5**: (i) a staggered conformation with two perpendicular planes was also found for the hydrazine groups (dihedral angle: <P2–N2–N3–Si2 = –90.1°), (ii) both nitrogen atoms of the hydrazine group are in an almost planar environment [Σ<(N2) = 359.98°, Σ<(N3) = 358.9°][9] and (iii) the azide groups are slightly *trans*-bent with an N–N–N angle of 171.7(5)°, which is in accordance with the structures of other covalent phosphorus azides.[24] Because of inversion symmetry, both azide groups adopt a *trans* position to each other. It is interesting to note that the longest chain composed of only pnictogen atoms in **6** consists of eleven pnictogens (eight N and three P atoms) compared to eight in compound **5** (six N and two P atoms). Moreover, **6** represents a rare example of a structurally characterised phosphorus azide involving a binary PN ring (Table 1).

Summary and Conclusions

Two different Staudinger reactions of thiophosphoryl triazide have been investigated: (i) with triphenylphosphane, PPh_3, and, (ii) with *N,N′,N′*-[tris(trimethyl)silyl]hydrazinediphenylphosphane, $(Me_3Si)_2N–(Me_3Si)N–PPh_2$ (**2**). While the reactions with PPh_3 utilising 1:1, 1:2 and 1:3 stoichiometries yield the single and double but not the triple Staudinger product, only the single Staudinger product was observed when $(Me_3Si)_2N–(Me_3Si)N–PPh_2$ was reacted. Even upon heating no further reaction of the remaining two azide groups with an excess of $(Me_3Si)_2N–(Me_3Si)N–PPh_2$ was detected. However, heating results in a partial intermolecular trimethylsilylazide elimination, which is combined with two condensation steps, yielding an eight-membered P_4N_4 ring (**6**). All four isolated Staudinger products represent new substituted phosphorus azides, are neither heat- nor shock-sensitive and, except for **6**, all can be prepared in large quantities (with yields >95%). Moreover, only a few neutral singly, doubly or multiply substituted phosphorus azides are known that have been structurally characterised (Table 1). Hence, the X-ray data of compound **5** and **6** may fill this gap.

Experimental Section

Caution: Although compounds **2**–**5** are kinetically stable compounds, they are nonetheless energetic materials and appropriate safety precautions should be taken, especially when these compounds are prepared on a larger scale. In the case of $SP(N_3)_3$ (**1**), special care has to be taken because of the extreme risk of explosion. Never handle this compound neat.

General Remarks: Solvents were freshly distilled, dried and stored under nitrogen. NMR: JEOL Eclipse 400 and 270 (^1H, ^{13}C chemical shifts refer to $\delta_{TMS} = 0.00$; ^{31}P to $\delta_{H_3PO_4(85\%)} = 0.00$). IR: Nicolet 520 FTIR (as KBr pellets or in Nujol mulls between KBr windows). Raman: Perkin–Elmer Spectrum 2000R NIR FT equipped with a Nd:YAG laser (1064 nm). CHN analyses: Analysator Elementar Vario EL. MS: Jeol MStation JMS 700. Melting points are uncorrected (Büchi B540). Thiophosphoryl triazide[30] and *N,N′,N′*-[tris(trimethyl)silyl]hydrazinediphenylphosphane[9] were prepared according to the procedures given in the literature.

Synthesis of 5: A solution of freshly prepared $SP(N_3)_3$ (0.242 g, 1.28 mmol) in acetonitrile (25 mL) was added to a solution of $Ph_2PN(TMS)N(TMS)_2$ (0.55 g, 1.28 mmol) in diethyl ether (50 mL) over a period of 1 h at ambient temperature. An immediate release of gas was observed. After the N_2 release stopped (about 2 h) the solvent was removed in vacuo and a white solid (**5**) was obtained. Complex **5** was purified by recrystallisation from an ether/acetonitrile mixture. $SP(N_3)_2[NP(Ph)_2N(TMS)N(TMS)_2]$ (**5**) (593.86) yield: 714 mg (94%) colourless crystals, m.p. 153 °C (decomposition). IR (KBr): $\tilde{\nu}$ = 3051 w, 2960 w, 2109 vs, 1588 w, 1482 w, 1436 s, 1260 vs, 1219 vs, 1177 s, 1111 vs, 1026 m, 996 m, 803 m, 777 m, 745 m, 718 s, 690 s, 675 m, 586 w, 529 s, 505 w cm^{-1}. Raman (200 mW, 25 °C, 100 scans): 3178 (4), 3146 (5), 3066 (100), 3052 (56), 2993 (18), 2958 (23), 2907 (84), 2255(2), 2153 (10), 2129 (7), 1591 (58), 1576 (21), 1442 (5), 1411 (6), 1316 (3), 1288 (17), 1267 (4), 1256 (4), 1184 (13), 1168 (9), 1107 (25), 1031 (40), 1002 (82), 935 (2), 858 (5), 762 (5), 728 (6), 692 (18), 650 (39), 619 (19), 598 (3), 569 (10), 542 (39), 523 (6), 506 (18), 381 (14), 345 (13), 314 (14), 296 (13), 270 (40), 239 (29), 191 (21), 168 (21), 139 (22) cm^{-1}. ^1H NMR (109 MHz, C_6D_6, 25 °C): δ = 0.01 (s, 18 H, $N[Si(CH_3)_3]N[Si(CH_3)_3]_2$), 0.37 (s, 9 H, $N[Si(CH_3)_3]N[Si(CH_3)_3]_2$), 7.5–8.0 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 3.90 (s, N[Si(CH$_3$)$_3$]$_2$), 4.54 (s, PN[Si(CH$_3$)$_3$]), 128.2 (d, $^1J_{CP}$ = 113.9 Hz, C$_{phenyl}$), 128.3 (d, $^3J_{CP}$ = 12.5 Hz, C$_{phenyl}$), 133.1 (d, $^4J_{CP}$ = 3.1 Hz, C$_{phenyl}$), 134.7 (d, $^1J_{CP}$ = 10.4 Hz, C$_{phenyl}$) ppm. ^{14}N NMR (28.9 MHz, C$_6$D$_6$, 25 °C): δ = –142 (N$_\beta$, $\Delta\nu_{1/2}$ 57 Hz), –163 (N$_\gamma$, $\Delta\nu_{1/2}$ 245 Hz), –285 (N$_\alpha$, $\Delta\nu_{1/2}$ 580 Hz) ppm. ^{29}Si{^{1}H} NMR (270 MHz, C$_6$D$_6$, 25 °C): δ = 12.92 (s, N[Si(CH$_3$)$_3$]$_2$), 18.15 (d, $^2J_{SiP}$ = 19.0 Hz, N[Si(CH$_3$)$_3$]) ppm. ^{31}P NMR (109 MHz, CH$_3$CN/Et$_2$O, 25 °C): δ = 46.6 (d, $^2J_{PP}$ = 34.3 Hz, SP(N$_3$)[NP(Ph)$_2$N(TMS)N(TMS)$_2$]), 26.5 (d, $^2J_{PP}$ = 34.3 Hz, SP(N$_3$)[NP(Ph)$_2$N(TMS)N(TMS)$_2$]) ppm. ^{31}P MAS NMR (25 kHz, 25°°C): 30.7 (SP(N$_3$)[NP(Ph)$_2$N(TMS)N(TMS)$_2$]), 51.0 (SP(N$_3$)[NP(Ph)$_2$N(TMS)N(TMS)$_2$]). MS (EI = 70 eV, >5%): *m/z* (%) = 593 (11) [M$^+$], 578 (40) [M$^+$ – CH$_3$], 493 (9), 492 (23) {NPNPh$_2$PN[Si(CH$_3$)$_3$]N[Si(CH$_3$)$_3$]$_2$$^+$}, 404 (7), 377 (8) [N$_2$(S)PNPh$_2$PNSi(CH$_3$)$_3$$^+$], 334 (6), 290 (9), 275 (6) [(Ph)$_2$PN$_2$Si(CH$_3$)$_3$ + 2H$^+$], 272 (20) [(Ph)$_2$PN$_2$Si(CH$_3$)$_3$ – H$^+$], 247 (10) {[Si(CH$_3$)$_3$]$_2$N – N[Si(CH$_3$)$_3$]$^+$}, 217 (11), 200 (5) [(Ph)$_2$PN – H$^+$], 199 (5), 185 (7) [(Ph)$_2$P – H$^+$], 183 (8), 175 (5) [(CH$_3$)$_3$SiNNSi(CH$_3$)$_3$ – H$^+$], 174 (28) [(CH$_3$)$_3$SiNNSi(CH$_3$)$_3$ – 2H$^+$], 146 (12) [Si(CH$_3$)$_3$ – Si(CH$_3$)$_3$$^+$], 135 (13) [SPN$_3P^+$], 122 (8), 77 (30) [Ph$^+$], 74 (12) [HSi(CH$_3$)$_3$$^+$], 73 (100) [Si(CH$_3$)$_3$$^+$]. C$_{21}H_{37}N_9P_2S_1Si_3$ (593.86): calcd. C 42.47, H 6.28, N 21.23, S 5.40; found C 42.60, H 6.30, N 21.42, S 5.95.

Supporting Information (see footnote on the first page of this article): Experimental details for the synthesis of **3**, **4** and **6**, and computational details.

X-ray Analyses of 5 and 6: Crystals of sufficient quality for X-ray structure determination were mounted on a glass fibre and the X-ray crystallographic data collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Selected bond lengths and angles are available in Table 3 and Table 4. All structures were solved by direct methods (structure solution program: SIR97[25] for **5** and **6**) and refined by full-matrix least-squares methods with SHELXL-97.[26] Hydrogen atoms were included at geometrically idealised positions and were not refined; the non-hydrogen atoms were refined anisotropically.

Crystallographic Data for 5: C$_{21}$H$_{37}$N$_9$P$_2$SSi$_3$, *fw* = 593.87, monoclinic, $P2_1/c$, a = 9.0514(1), b = 18.2759(3), c = 18.7805(3) Å, α = 90.0, β = 96.4276(8), γ = 90.0°, V = 3087.19(8) Å^3, Z = 4, $\rho_{calcd.}$ = 1.278 g/cm^3, μ = 0.353 mm^{-1}, λ(Mo-K_α) = 0.71073 Å, T = 200 K, 36065 reflections collected, 6983 independent reflections, R_{int} = 0.092, 5381 observed reflections, R_1 = 0.0469, wR_2 = 0.1308.

Crystallographic Data for 6: C$_{36}$H$_{56}$N$_{12}$P$_4$S$_2$Si$_4$, *fw* = 957.29, monoclinic, $P2_1/n$, a = 11.6491(3), b = 13.8277(4), c = 15.1723(5) Å, α = 90.0, β = 95.776(1), γ = 90.0°, V = 2431.5(1) Å^3, Z = 2, $\rho_{calcd.}$ = 1.308 g/cm^3, μ = 0.381 mm^{-1}, λ(Mo-K_α) = 0.71073 Å, T = 200 K, 5520 reflections collected, 28073 independent reflections, R_{int} = 0.080, 3880 observed reflections, R_1 = 0.0558, wR_2 = 0.1364.

CCDC-283470 (for **5**) and -283471 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: The structural data of all considered species were calculated using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[27] For all elements a standard 6-31G(d,p) basis set was used. Comparison with experimental data shows differences in bond lengths no larger than 0.01–0.02 Å.[12a] As frequency analyses were not possible because of the large size of all species at the B3LYP level, PM3 optimised structures (stationary points) were characterised by a frequency analysis displaying only positive frequencies. NBO analyses[13a,28] were carried out to investigate the bonding in all molecules at the SCF level utilising the optimised B3LYP/6-31G(d,p) geometry and RHF orbitals. Also, NBO population analysis for **5** and **6** was carried out with the structure fixed at the position determined from X-ray analysis of **5** and **6** to investigate the bonding and hybridisation in this experimentally observed species. The computed geometrical parameters for all molecules, relative energies, details of the NBO analyses and absolute energies are given as Supporting Information. The computed frequencies can be obtained from the authors. It should be emphasised that the computation was carried out for a single, isolated (gas-phase) molecule. There may well be significant differences among gas-phase, solution and solid-state data.

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