The difference regarding the reactivity of the silanides Na[Si t Bu $_3$] and Na[SiPhtBu $_2$] towards white phosphorus

Andreas Lorbach, Sven Breitung, Inge Sanger, Frauke Schodel, Michael Bolte, Matthias Wagner, Hans-Wolfram Lerner*

Institut fur Anorganische Chemie, Goethe-Universitat Frankfurt am Main, Max-von-Laue-Str. 7, 60438 Frankfurt, Germany

A B S T R A C T

The sodium tetraphosphenediides Na $_2$ [t Bu $_2$ RSiP–P=P–PSi t RtBu $_2$] (R = t Bu, Ph) were formed when P $_4$ was treated with two equivalents of the silanides Na[Si t RtBu $_2$] in thf. Whereas treatment of P $_4$ with three equivalents of Na[SiPhtBu $_2$] in thf gave the tetraphosphide Na $_3$ [P(PSiPhtBu $_2$) $_3$] as main product (along with, e.g., Na $_2$ [PSiPhtBu $_2$], Na $_2$ [t Bu $_2$ PhSiP–P=P–PSiPhtBu $_2$], and Na $_2$ [P $_5$ (SiPhtBu $_2$) $_3$]). However, no tetraphosphide Na $_3$ [P(Si t Bu $_3$) $_3$] was formed by the reaction of P $_4$ with three equivalents of Na[Si t Bu $_3$] in thf. The triphosphide Na[t Bu $_2$ PhSiP–P=P–PSiPhtBu $_2$] could be obtained together with Na[PHSiPhtBu $_2$] by protolysis of Na $_3$ [P(PSiPhtBu $_2$) $_3$]. When a mixture of a 3:1 reaction of Na[SiPhtBu $_2$] and P $_4$ was heated to 100 °C *in vacuo*, {Na[P(SiPhtBu $_2$) $_2$]} $_2$ was generated along with Na $_2$ [PSiPhtBu $_2$] and P $_4$. Single crystals of Na[P(SiPhtBu $_2$) $_2$] were grown from a heptane solution at room temperature (monoclinic space group C2/c).

Keywords:
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1. Introduction

Activation of white phosphorus has received a renewed interest in recent years [1,2]. In several reports information about the reactivity of P $_4$ towards nucleophilic agents has been documented [1–16]. Previously we have reported that the products of the reaction between P $_4$ and the tri-*tert*-butylsilanides (supersilanides) M[Si t Bu $_3$] (M = Li, Na, K) [12,17] depend strongly on the stoichiometry and solvent [6–12]. Using the reactants in molar ratios from 1:2 to 1:4, different phosphides were formed, as depicted in Scheme 1: (i) the supersilylated tetraphosphenediides M $_2$ [**1a**] (M = Li, Na, K) were obtained from the reaction of P $_4$ and M[Si t Bu $_3$] (M = Li, Na, K) in a molar ratio of 1:2 in thf [7,8], (ii) the supersilylated octaphosphides M $_4$ [**2a**] (M = Na, K), however, were also synthesized in a 1:2 stoichiometry but in weakly polar solvents (heptane, t BuOMe, etc.) [10,12], (iii) the synthesis of the tetraphosphides M $_3$ [**3a**] (M = Li, Na) and Na $_3$ [P(PSiPhtBu $_2$) $_3$] (Na $_3$ [**3b**]) was achieved by the reaction of P $_4$ with the silanides M[Si t Bu $_3$] (M = Li, Na) and Na[SiPhtBu $_2$] [9] in a 1:3 stoichiometry in benzene, however, in thf M $_3$ [**3a**] (M = Li, Na, K) are unstable and thereby, (iv) M[**4a**] and M $_2$ [PSi t Bu $_3$] (M = Li, Na, K) were formed [8,9] and (v) at last the pentaphosphide M $_2$ [**5a**] could be synthesized by degradation of the corresponding octaphosphides M $_4$ [**2a**] with M[Si t Bu $_3$] (M = Na, K) or was directly accessible by treating of P $_4$ with four equivalents of Na(thf) $_2$ [Si t Bu $_3$] in benzene [10]. Very recently we

have discovered that white phosphorus reacts with three molar equivalents of Li[Mes] [16] in benzene forming the phosphide Li $_3$ [P(PMes) $_3$] (Li $_3$ [**3c**]) that has been produced in analogous 1:3 reactions of P $_4$ with the silanides M[Si t Bu $_3$] [12,17] (M = Li, Na) and Na[SiPhtBu $_2$] [18,19,16]. In contrast to the 1:3 reactions of P $_4$ with the silanides M[Si t Bu $_3$] [12,17] (M = Li, Na) and Na[SiPhtBu $_2$] [18,19] or with Li[Mes] [16] in benzene, which gave the tetraphosphides M $_3$ [**3a**] (M = Li, Na), Na $_3$ [**3b**], and Li $_3$ [**3c**] [9,16] treatment of P $_4$ with three equivalents of K[Si t Bu $_3$] in thf first led to the formation of K $_2$ [**1a**] and K $_4$ [**2a**] [8]. Finally K[**4a**] and K $_2$ [PSi t Bu $_3$] were generated thereby [8].

In this context it should be noted that normally reactions of the phosphides M $_x$ [**1a–5a**] with electrophilic reactants take place with a rearrangement of their P-core.¹ However, in some cases a cation exchange could be carried out without degradation of the P-cluster [10,21,22].

In the literature it was reported that tetrazane H $_6$ N $_4$, a homologous compound of the tetraphosphanes M $_3$ [**3a–c**], decomposes spontaneously to triazene NH $_2$ –N=N–NH and ammonia by an analogous way as mentioned in Scheme 1 for Na $_3$ [**3a**] [23,24]. It was found that the unsaturated nitrogen–hydrogen compounds are very temperature-sensitive (Scheme 2; e.g., decomposition temperatures: –180 °C (HN=NH), –30 °C (*trans*-H $_2$ N–N=N–NH $_2$)) [25–29]. Especially triazene HN=NH and *cis*-2-tetrazene H $_2$ N–N=N–NH $_2$ are very unstable (decomposition temperatures

* Corresponding author. Tel.: +49 69 79829152; fax: +49 69 79829260.
E-mail address: lerner@chemie.uni-frankfurt.de (H.-W. Lerner).

¹ Regarding the reaction of the phosphides M $_x$ [**1a–5a**] with nucleophilic reactants (see Ref. [20]).

Scheme 1. Degradation of P_4 with the supersilanides $M[Si(t-Bu)_3]$ ($M = Li, Na, K$).

Scheme 2. Formation and decomposition of nitrogen-hydrogen compounds. (i) $-H_2$; (ii) $\times 2, -N_2$; (iii) 1. $Me_3SiCl-HCl$, 2. $+CF_3CO_2H-CF_3CO_2SiMe_3$ in CH_2Cl_2 at $-78^\circ C$; (iv) $-N_2$ (base catalysed); (v) in CH_2Cl_2 (97%, acid catalysed); and (vi) $+Fe^{3+}, -Fe^{2+}, -H^+$; (vii) $-NH_3$.

below $-200^\circ C$ [23,24,30]. However, it was proved that their silyl derivatives are thermodynamically more stable than the unsaturated nitrogen-hydrogen compounds [28,29,31–41]. In the course of our investigation into unsaturated nitrogen compounds, we were able to isolate several silylated triazene and *cis*-2-tetrazene derivatives [36–38]. The triazenides $M[t-Bu_3SiN-N=NSiRtBu_2]$ ($M = Li, Na$; $R = Me, tBu$) are accessible from the reaction of tBu_2R-SiN_3 ($R = Me, tBu$) with the silanides $MSiRtBu_3$ ($M = Li, Na$) at $-78^\circ C$ [39]. However, at room temperature the triazenides $M[t-Bu_3SiN-N=NSiMeRtBu_2]$ ($M = Li, Na$) decompose with liberation of N_2 to give the silylamides $M[N(SiMeRtBu_2)(SiRtBu_3)]$ ($M = Li, Na$) [39].

In this paper, we present a comparative study of the reactions of P_4 with the sodium silanides $Na[Si(t-Bu)_3]$ and $Na[SiPh(t-Bu)_2]$ [12] in molar ratios of 1:3 in *thf*. In addition, we report here the preparation and the spectroscopic properties of $Na_2[t-Bu_2PhSiP-P=P-SiPh(t-Bu)_2]$ ($Na_2[1b]$) and $Na[t-Bu_2PhSiP-P=P-SiPh(t-Bu)_2]$ ($Na[4b]$), respectively. Finally the crystal structure of the sodium monophosphanide $\{Na[P(SiPh(t-Bu)_2)_2]\}_2$ is described.

2. Experimental

2.1. General remarks

All experiments were carried out under dry argon or nitrogen using standard Schlenk and glove-box techniques. Solvents were distilled from sodium/benzophenone under a dry argon atmosphere. $Na[Si(t-Bu)_3]$ [12,17], $Na[SiPh(t-Bu)_2]$ [18,19], and $Na_3[3b]$ [9] were prepared according to the published procedures. All other starting materials were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400 spectrometer. The ^{29}Si spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from *t*Bu protons. Mass spectrometry was performed with a Fisons VG Platform II. UV-Vis spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. Elemental analyses were performed at the microanalytical laboratories of the University of Frankfurt.

2.2. Synthesis of $\text{Na}_2[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($\text{Na}_2[\mathbf{1b}]$)

A solution of $\text{Na}[\text{SiPh}(\text{tBu})_2]$ (8.80 mmol) in 20 mL thf was added dropwise to a cooled solution (-78°C) of P_4 (4.40 mmol) in 44 mL thf. When the reaction solution was warmed up to room temperature, the solution underwent a color change to deep red. The tetraphosphenediide $\text{Na}_2[\mathbf{1b}]$ was formed thereby quantitatively, as determined by ^{31}P NMR spectroscopy. This solution of $\text{Na}_2[\mathbf{1b}]$ was used for further investigations.

$\text{Na}_2[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($[\text{Na}_2[\mathbf{1b}]]$): ^1H NMR (250.132 MHz, d_8 -thf, internal TMS): δ 1.06 (br, 36H *t*Bu), 7.14–7.65 (m, 10H *m/o/p*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.467 MHz, d_8 -thf, external H_3PO_4 ; see Fig. 1) [37]. $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.608 MHz, d_8 -thf, external TMS): δ 15.8 (m). MS (ESI $^+$): m/z (%) = 681.7 (13.2), 680.8 (46.9), 679.8 (100.0) $[\text{tBu}_2\text{PhSiPNa}(\text{thf})-\text{P}=\text{P}-\text{PNaSiPh}(\text{tBu})_2]^+$, calcd $[\text{tBu}_2\text{PhSiPNa}(\text{thf})-\text{P}=\text{P}-\text{PNaSiPh}(\text{tBu})_2]^+$ 682.2 (16.6), 681.3 (45.4), 680.3 (100.0).

All volatiles of the red solution of $\text{Na}_2[\mathbf{1b}]$ (0.5 mmol) in thf (5 mL) were removed *in vacuo*. An orange solid remained, which could be extracted into C_6D_6 . The ^{31}P NMR spectrum of the C_6D_6 solution showed signals which could be assigned to $\text{Na}_4[\mathbf{2b}]$.

$\text{Na}_4[\text{P}_4(\text{SiPh}(\text{tBu})_2)_4]$ ($\text{Na}_4[\mathbf{2b}]$): ^1H NMR (250.132 MHz, d_8 -thf, internal TMS): δ 1.14 (br, 72H *t*Bu), 7.14–7.60 (m, 20H *m/o/p*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.467 MHz, d_8 -thf, external H_3PO_4): δ 22.1 (m, $\text{P}_4(\text{PNaSiPh}(\text{tBu})_2)_4$), -185.6 (m, $\text{PNaSiPh}(\text{tBu})_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.608 MHz, d_8 -thf, external TMS): δ 13.0 (m). MS (ESI $^+$): m/z = 1359.4 $[\text{Na}_4(\text{thf})_2\text{P}_4(\text{SiPh}(\text{tBu})_2)_4]^+$, calcd for $[\text{Na}_4(\text{thf})_2\text{P}_4(\text{SiPh}(\text{tBu})_2)_4]^+$ 1360.5.

Remark: When a solution of tetraphosphenediide $\text{Na}_2[\mathbf{1b}]$ (1 mmol) in thf (10 mL) was treated with an excess of trifluoroacetic acid (2.5 mmol) in thf (5 mL) the tetraphosphenediide $\text{Na}_2[\mathbf{1b}]$ was converted into the literature-known [42] phosphane $\text{tBu}_2\text{PhSiPH}_2$ and up to now not exactly identified polyphosphanes, as determined by ^{31}P NMR spectroscopy. At $80^\circ\text{C}/0.01$ mbar pure $\text{tBu}_2\text{PhSiPH}_2$ was distilled as a colorless oil (yield 40%). $\text{tBu}_2\text{PhSiPH}_2$: ^1H NMR (250.132 MHz, C_6D_6 , internal TMS): δ 1.06 (d, $^4J_{\text{PH}} = 0.49$ Hz, 18H *t*Bu), 1.42 (d, $^1J_{\text{PH}} = 187.3$ Hz, 2H), 7.14 (m, 12H *o/p*-Ph), 7.67 (m, 8H *m*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , internal TMS): δ 21.7 (d, $^2J_{\text{CP}} = 5.3$ Hz, CMe_3), 29.9 (d, $^3J_{\text{PC}} = 2.0$ Hz, CMe_3), 128.5 (s; *m*-Ph), 129.9 (s; *p*-Ph), 136.2 (d, $^2J_{\text{CP}} = 7.3$ Hz; *i*-Ph), 136.7 ($^3J_{\text{CP}} = 5.5$ Hz; *o*-Ph). ^{31}P NMR (121.467 MHz, C_6D_6 , external H_3PO_4): -266.5 (t, $^1J_{\text{PH}} = 187.3$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.608 MHz, C_6D_6 , external TMS): δ 16.8 (d). *Anal. Calc.* for

$\text{C}_{14}\text{H}_{25}\text{PSi}$ (252.41): C, 66.62; H, 9.98. Found: C, 65.45; H, 9.80. MS (ESI $^+$): m/z = 252.0 $[\text{M}]^+$, calcd for $[\text{M}]^+$ 252.2.

2.3. Reaction of P_4 with three equivalents of $\text{Na}[\text{SiPh}(\text{tBu})_2]$

A solution of $\text{Na}[\text{SiPh}(\text{tBu})_2]$ (0.60 mmol) in 2 mL thf was combined with a solution of P_4 (0.20 mmol) in 2 mL thf. After stirring for 12 h at room temperature the ^{31}P NMR spectrum of the reaction solution showed resonances due to the tetraphosphide $\text{Na}_3[\text{P}(\text{SiPh}(\text{tBu})_2)_3]$ ($\text{Na}_3[\mathbf{3b}]$) (main product), the tetraphosphenediide $\text{Na}_2[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($\text{Na}_2[\mathbf{1b}]$), the octaphosphide $\text{Na}_4[\text{P}_8(\text{SiPh}(\text{tBu})_2)_4]$ ($\text{Na}_4[\mathbf{2b}]$), the pentaphosphide $\text{Na}_2[\text{P}_5(\text{SiPh}(\text{tBu})_2)_3]$ ($\text{Na}_2[\mathbf{5b}]$), and the monophosphandide $\text{Na}_2[\text{PSiPh}(\text{tBu})_2]$ (ratio see Table 1). In addition very small signals appeared which could be assigned to the triphosphide $\text{Na}[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($\text{Na}[\mathbf{4b}]$). After storing the reaction solution for 2 weeks at room temperature the ^{31}P NMR spectrum revealed that the amount of the pentaphosphide $\text{Na}_2[\mathbf{5b}]$ increased whereas the signals of the octaphosphide $\text{Na}_4[\mathbf{2b}]$ had disappeared completely. During storing this solution for 2 months at room temperature an orange solid precipitated. This solid consists of the pentaphosphide $\text{Na}_2[\mathbf{5b}]$ as verified by ^{31}P NMR spectroscopy. Yield: 37 mg (10%). Selected data for $\text{Na}_2[\mathbf{5b}]$ see above.

$\text{Na}_2[\text{P}_3(\text{SiPh}(\text{tBu})_2)(\text{PSiPh}(\text{tBu})_2)_2]$ ($\text{Na}_2[\mathbf{5b}]$): ^1H NMR (250.132 MHz, d_8 -thf, internal TMS): δ 1.10 (br, 36H *t*Bu), 1.20 (br, 18H *t*Bu), 7.18–7.60 (m, 15H *m/o/p*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.467 MHz, d_8 -thf, external H_3PO_4 ; see Fig. 3) [37]. $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.608 MHz, d_8 -thf, external TMS): δ 23.0 (m, $\text{P}_3\text{SiPh}(\text{tBu})_2$), 6.5 (m, $\text{NaPSiPh}(\text{tBu})_2$). MS (ESI $^+$): m/z = 1002.7 $[\text{P}_3(\text{SiPh}(\text{tBu})_2)(\text{PNa}(\text{thf})\text{SiPh}(\text{tBu})_2)_2]^+$, calcd for $[\text{P}_3(\text{SiPh}(\text{tBu})_2)(\text{PNa}(\text{thf})\text{SiPh}(\text{tBu})_2)_2]^+$ 1002.4.

2.4. Synthesis of $\text{Na}[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($\text{Na}[\mathbf{4b}]$)

When a solution of $\text{Na}_3[\mathbf{3b}]$ (1.2 mmol) in 5 mL benzene was stirred for 4 weeks at room temperature in a glove box the reaction mixture underwent a color change to purple. Two products were formed: the triphosphide $\text{Na}[\mathbf{4b}]$ and $\text{Na}[\text{PHSiPh}(\text{tBu})_2]$. The monophosphanide $\text{Na}[\text{PHSiPh}(\text{tBu})_2]$ was separated by filtration. Evaporation of the solvent yielded the triphosphide $\text{Na}[\mathbf{4b}]$ as a purple solid (47%). Several attempts to determine the structure failed.

$\text{Na}[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSiPh}(\text{tBu})_2]$ ($\text{Na}[\mathbf{4b}]$): ^1H NMR (250.132 MHz, d_8 -thf, internal TMS): δ 1.07 (br, 36H *t*Bu), 7.14–7.60 (m, 10H *m/o/p*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.296 MHz, d_8 -thf, external H_3PO_4 ; see

Fig. 1. Observed and calculated ^{31}P NMR spectra of $\text{Na}_2[\mathbf{1b}]$. Chemical shifts and coupling constants [Hz] of $\text{Na}_2[\mathbf{1b}]$: δ 397.4, δ -44.3, $^1J_{\text{P}(2)\text{P}(3)} = -502.1$, $^1J_{\text{P}(1)\text{P}(2)} = -432.3$, $^2J_{\text{P}(1)\text{P}(3)} = -34.2$, $^3J_{\text{P}(1)\text{P}(4)} = 185.4$.

Table 1Products of the reaction between P₄ and three molar equivalents of Na[SiRtBu₂] (R = tBu, Ph) in thf (ratio in% P).

P ₄ + equivalents of 3 Na[SiRtBu ₂]			P ₄ + equivalents of 3 Na[SiPhtBu ₂]		
Phosphide	$\delta(^{31}\text{P})^a$	%P ^b	Phosphide	$\delta(^{31}\text{P})^a$	%P ^b
Na ₂ [1a] [7]	400.0, −45.2	21.2 (35.8)	Na ₂ [1b]	397.4, −44.3	9.9 (36.0)
Na ₄ [2a] [10]	24.1, −177.3	0 (11.8)	Na ₄ [2b]	22.1, −185.6	0 (5.8)
Na ₃ [3a] [9]	— ^c	0 (0)	Na ₃ [3b] [9]	−34.4, −110.3	43.9 (36.6)
Na[4a] [43]	732.5, 212.5	17.7 (12.3)	Na[4b]	713.0, 207.6	0.4 (0)
Na ₂ [5a] [11]	−93.4, −179.6, −240.3	45.5 (31.5)	Na ₂ [5b]	−88.9, −181.6, −242.8	31.5 (19.2)
Na ₂ [PSiRtBu ₃] [9]	404.4	15.6 (8.4)	Na ₂ [PSiPhtBu ₂]	−408.6	13.3 (2.4)
Na[P(SiRtBu ₂) ₂] [21]	— ^d	0 (0)	Na[P(SiPhtBu ₂) ₂]	−351.0	1.0 (0)

^a In d₈-thf after 2 weeks.^b In brackets after 12 h.^c $\delta(^{31}\text{P}) = -11.7, -100.7$, see Ref. [9].^d $\delta(^{31}\text{P}) = -345.4$, see Ref. [21].

Fig. 2) [37]. ²⁹Si{¹H}NMR (59.608 MHz, d₈-thf, external TMS): δ 12.8 (m). MS (ESI[−]): m/z (%) = 532.7 [tBu₂PhSiP=P=PSiPhtBu₂][−], calcd for [tBu₂PhSiP=P=PSiPhtBu₂][−] 531.2.

Na[PHSiPhtBu₂]: ¹H NMR (250.132 MHz, d₈-thf, internal TMS): δ 1.02 (br, 18H tBu), 7.14–7.65 (m, 5H *m/o/p*-Ph). ³¹P NMR (101.296 MHz, d₈-thf, external H₃PO₄): δ −331.3 (d, ¹J_{PH} = 153.3 Hz). ²⁹Si{¹H}NMR (59.608 MHz, d₈-thf, external TMS): δ 27.4 (d, ¹J_{PSi} = 69.7 Hz).

2.5. Synthesis of {Na[P(SiPh(tBu)₂)₂]}₂

A solution of Na[SiPhtBu₂] (3.00 mmol) in 10 mL thf was added dropwise to a cooled solution of P₄ (1.00 mmol) in 10 mL thf. The reaction solution was warmed up to room temperature. The ³¹P NMR spectrum of the reaction solution indicated that the phosphides mentioned in Table 1 were formed. All volatiles were removed *in vacuo* at 100 °C/0.01 mbar. The yellow residue was extracted with heptane (5 mL) and filtered. The filter cake was washed with heptane (4 × 2 mL) and the filtrate was concentrated to 2 mL, during which time colorless crystals of {Na[P(SiPhtBu₂)₂]}₂ were deposited. Yield: 0.25 g (17%). The filter cake could be dissolved in thf. The ³¹P NMR spectrum of the dissolved filter cake revealed resonances due to Na[PH(SiPhtBu₂)₂] (δ = −311.3) and Na₂[P(SiPhtBu₂)₂] (δ = −408.6).

{Na[P(SiPhtBu₂)₂]}₂: ¹H NMR (C₆D₆, internal TMS): ¹H NMR (250.132 MHz, d₈-thf, internal TMS): δ 1.14 (br, 36H tBu), 7.14–7.65 (m, 10H *m/o/p*-Ph). ³¹P NMR (101.296 MHz, d₈-thf, external H₃PO₄): δ −351.0 (d, ¹J_{PH} = 153.3 Hz). ²⁹Si{¹H}NMR (59.608 MHz, d₈-thf, external TMS): δ 21.4 (d, ¹J_{PSi} = 81.1 Hz).

Remark: When a solution {Na[P(SiPhtBu₂)₂]}₂ (0.1 mmol) in thf (1 mL) was treated with an excess of trifluoroacetic acid (0.3 mmol), the monophosphanide {Na[P(SiPhtBu₂)₂]}₂ was converted into the phosphane HP(SiPhtBu₂)₂, as determined by NMR spectroscopy.

HP(SiPhtBu₂)₂: ¹H NMR (250.132 MHz, C₆D₆, internal TMS): δ 1.06 (br, 36H tBu), 7.14–7.70 (m, 10H *m/o/p*-Ph). ³¹P NMR (121.467 MHz, C₆D₆, external H₃PO₄): −269.5 (d, ¹J_{PH} = 215.2 Hz). ²⁹Si{¹H}NMR (59.608 MHz, d₈-thf, external TMS): δ 19.4 (d, ¹J_{PSi} = 57.9 Hz). *Anal.* Calc. for C₂₈H₄₇PSi₂ (470.82): C, 71.43; H, 10.06. Found: C, 70.83; H, 9.83.

2.6. Reaction of P₄ with three equivalents of Na[SiRtBu₃]

A solution of Na[SiRtBu₃] (7.50 mmol) in 19 mL thf was combined with a solution of P₄ (2.50 mmol) in 25 mL thf. After stirring for 12 h at room temperature, the ³¹P NMR spectrum of the reaction solution showed resonances due to the tetraphosphenediide Na₂[tBu₃SiP=P=PSiRtBu₃] [7] (Na₂[**1a**]), the octaphosphide Na₄[P₈(SiRtBu₃)₄] [10] (Na₄[**2a**]), the triphosphide Na[tBu₃SiP=P=PSiRtBu₃] [43] (Na[**4a**]), the pentaphosphide Na₂[P₅(SiRtBu₃)₃] [11] (Na₂[**5a**]), and

Table 2Crystal data and refinement details for the monophosphanide {Na[P(SiPhtBu₂)₂]}₂.

	{Na[P(SiPhtBu ₂) ₂]} ₂
Empirical formula	C ₅₆ H ₉₂ Na ₂ P ₂ Si ₄
Formula weight	985.58
<i>T</i> (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
<i>a</i> (Å)	11.685(2)
<i>b</i> (Å)	33.118(7)
<i>c</i> (Å)	16.155(3)
α (°)	90
β (°)	110.37(3)
γ (°)	90
<i>V</i> (Å ³)	5861(2)
<i>Z</i>	4
Density calculated (g cm ^{−3})	1.117
<i>F</i> (000)	2144
μ (mm ^{−1})	0.204
Index ranges	−13 ≤ <i>h</i> ≤ 13 −39 ≤ <i>k</i> ≤ 35 −19 ≤ <i>l</i> ≤ 15
Crystal size (mm ³)	0.33 × 0.11 × 0.03
Number of reflections collected	11 342
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0728, 0.1001
Data/restraints/parameter	5077/0/290
GOF on <i>F</i> ²	0.836
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.1797, <i>wR</i> ₂ = 0.1301
Largest diff peak and hole (e Å ^{−3})	0.223 and −0.272

the monophosphanediide Na₂[PSiRtBu₃] [9] (ratio see Table 1). However, no signals of the tetraphosphide Na₃[P(PSiRtBu₃)₃] [9] (Na₃[**3a**]) were recorded. After storing the reaction solution for 2 weeks at room temperature, the ³¹P NMR spectrum revealed that the amount of the pentaphosphide Na₂[**5a**] [11] increased whereas the signals of the octaphosphide Na₄[**2a**] [10] had disappeared completely.

2.7. Crystal structure determination

Data collection: Stoe-IPDS-II diffractometer, graphite-monochromated Mo K α radiation; *T* = 173 K. Empirical absorption correction using MULABS, structure solution by direct methods, structure refinement by full-matrix least-squares on *F*² with SHELXL-97 [44]. Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. Crystallographic data for the structure are given in Table 2.

3. Results and discussion

The reaction of P₄ with two equivalents of M[SiRtBu₃] (M = Li, Na, K) or Na[SiPhtBu₂] in thf leads to the corresponding

tetraphosphenediides $M_2[1a]$ ($M = Li, Na, K$) and $Na_2[1b]$, respectively, which could be dimerized in weakly polar solvents to the corresponding octaphosphides. We found that white phosphorus reacts with three molar equivalents of $Na[SiPhBu_2]$ in thf, forming the same types of phosphides, that has been produced in the 1:3 reaction of P_4 with $K[SiPhBu_2]$ in thf. After 1 h, the silanide $Na[SiPhBu_2]$ was completely consumed as determined by NMR spectroscopy. In the ^{31}P NMR spectrum of the reaction solution signals appeared which could be assigned to the tetraphosphenediide $Na_2[1a]$, the octaphosphide $Na_4[2a]$, the triphosphide $Na[4b]$, the pentaphosphide $Na_2[5a]$, and the monophosphandiide $Na_2[6a]$ (Table 1). However, the resonances of the tetraphosphide $Na_3[3a]$ which is the main product in benzene, could not be detected thereby. Interestingly, when the reaction mixture was stored at ambient temperature for several weeks, in the ^{31}P NMR spectrum the signals of $Na_2[1a]$ and $Na_4[2a]$ became smaller and the signals of the triphosphide $Na[4b]$ and the pentaphosphide $Na_2[5a]$ increased.

When P_4 in thf was treated with three molar equivalents of $Na[SiPhBu_2]$, the reaction mixture underwent a color change to red. In contrast to the pathway of the 1:3 reaction between P_4 and $Na[SiPhBu_2]$ in thf, this reaction produces the tetraphosphide $Na_3[3b]$ as its main product. In the ^{31}P NMR spectrum of the reaction mixture resonances due to the main product $Na_3[3b]$, the tetraphosphenediide $Na_2[1b]$, the octaphosphide $Na_4[2b]$, the pentaphosphide $Na_2[5b]$, and the monophosphandiide $Na_2[6b]$ were observed (Table 1). In addition very small signals appeared which could be assigned to the triphosphide $Na[4b]$. The tetraphosphenediide $Na_2[1b]$, the triphosphide $Na[4b]$, and the pentaphosphide $Na_2[5b]$, were identified unambiguously by ^{31}P NMR spectroscopy. After storing this solution for 2 weeks at room temperature, the ^{31}P NMR spectrum revealed that the amount of the pentaphosphide $Na_2[5b]$ increased whereas the resonances due to the octaphosphide $Na_4[2b]$ had disappeared completely.

The supersilylated tetraphosphides $M_3[3a]$ ($M = Li, Na, K$), which has been formed by the reaction of P_4 with three molar equivalents of $M[SiPhBu_2]$ ($M = Li, Na, K$), apparently underwent an elimination reaction in thf to give the triphosphides $M[4a]$ ($M = Li, Na, K$) and $M_2[PSiPhBu_2]$ [8,9]. By contrast the corresponding tetraphosphide $Na_3[3b]$ with the less bulky di-*tert*-butylphenylsilyl substituent is more stable. Therefore no thermolysis of $Na_3[3b]$ takes place under similar reaction conditions.

However, when a mixture of a 3:1 reaction of $Na[SiPhBu_2]$ and P_4 was heated to 100 °C *in vacuo*, $\{Na[P(SiPhBu_2)_2]\}_2$ was generated together with $Na_2[PSiPhBu_2]$ and P_4 . The formation of these

Scheme 3. Reaction of P_4 with the sodium silanide $Na[SiPhBu_2]$ in a molar ratio of 1:3. (i) in benzene; (ii) in thf, subsequent heating to 100 °C at 0.01 mbar, $-Na_2[PSiPhBu_2]$; and (iii) stirring in benzene for 4 weeks at room temperature, $+H$, $-Na[HSiPhBu_2]$.

Fig. 2. ^{31}P NMR spectrum of $Na[4b]$. Chemical shifts and coupling constants [Hz] of $Na[4b]$: δ 713.0, δ 207.6, $^1J_{P(A)P(X)} = 542.6$.

products raised the question whether $\{Na[P(SiPhBu_2)_2]\}_2$ and P_4 were produced via $Na[4b]$ in an analogous way as found in the thermolysis of the triazenides $M[tBu_3SiN=N=NSiRtBu_2]$ ($R = Me, tBu$) [39].

The triphosphide $Na[4b]$ could be prepared by transformation of $Na_3[3b]$, as shown in Scheme 3. When a solution of $Na_3[3b]$ in benzene was stirred for 4 weeks at room temperature in a glove box the reaction mixture underwent a color change to purple. Two products were formed: the triphosphide $Na[4b]$ and $Na[PHSiPhfBu_2]$. The monophosphanide $Na[PHSiPhfBu_2]$ could be separated from $Na[4b]$ by precipitation. The triphosphide $Na[4b]$ was identified unambiguously by its ^{31}P NMR spectrum (Fig. 2). However, neither heating $Na[4b]$ to 100 °C for 10 h *in vacuo* nor heating a thf solution of $Na[4b]$ in a sealed NMR tube to 120 °C for 2 days led to decomposition of $Na[4b]$. Obviously, under these conditions no degradation reaction of $Na[4b]$ has taken place.²

NMR spectra: Generally, the NMR spectra of sodium phosphides $Na_x[1b-5b]$ resemble those of the supersilylated alkali metal phosphides $M_x[1a-5a]$ [6–12,21,43].

The ^{29}Si as well as ^{31}P NMR spectrum of $Na_2[1b]$ is comparable with those of the supersilylated alkali metal tetraphosphenediides $M_2[1a]$ ($M = Li, Na, K, Rb, Cs$) [7]. The $^{31}P\{^1H\}$ NMR spectra of all these tetraphosphenediides show multiplets with the splitting pattern of an $AA'XX'$ spin system. As shown in Fig. 1, the signals of the P(1) and P(4) nuclei of $Na_2[1b]$ are broadened, due to coupling of P(1) and P(4) with sodium nuclei. In contrast to the ^{31}P NMR spectra of neutral tetraphosphene derivatives [4,5], which reveal two sets of signals suggesting an equilibrium of *cis*- and *trans*-tetraphosphene isomers in solution, we found that only one set of signals could be recorded in the ^{31}P NMR spectrum of the ion-separated tetraphosphenediide $[Na(18-crown-6)(thf)_2]_2[1a]$ as well as in that of the corresponding contact-ion pair $Na_2[1a]$ [7].

Further information about the bonding situation in alkali metal tetraphosphenediides $M_2[1a]$ and $Na_2[1b]$ were obtained from the PP coupling constants. The ^{31}P NMR spectra of the ion-separated tetraphosphenediide $[Na(18-crown-6)(thf)_2]_2[1a]$ and of the contact-ion pair $Na_2[1a]$ reveal different coupling constants [7]. The values of the coupling constants $^1J_{P(2)P(3)}$ and $^1J_{P(1)P(2)}$ of $[Na(18-crown-6)(thf)_2]_2[1a]$ are significantly higher than those of the

² Thermolysis of $Na[4b]$ at temperature higher than 150 °C gives among other products $Na[P(SiPhBu_2)_2]$, as determined by ^{31}P NMR spectroscopy.

contact-ion pair $\text{Na}_2[\mathbf{1a}]$ but the values of both tetraphosphenediides lie in the double-bond region. This predicts a bonding situation as found in 1,3-butadiene. However, the increase in the $^3J_{\text{P}(1)\text{P}(4)}$ coupling constants going from $[\text{Na}(\text{18-crown-6})(\text{thf})_2][\mathbf{1a}]$ to the contact-ion pair $\text{Na}_2[\mathbf{1a}]$ is significant and is presumably caused by a different *s-cis*/*s-trans* rotamer relation of the contact-ion pair $\text{Na}_2[\mathbf{1a}]$ and $[\text{Na}(\text{18-crown-6})(\text{thf})_2][\mathbf{1a}]$. We found a strong correlation between the value of $^3J_{\text{P}(1)\text{P}(4)}$ constants and the molecular structure of tetraphosphene derivatives. Large values of $^3J_{\text{P}(1)\text{P}(4)}$ constants suggest the existence of *s-cis*-rotamers or *cis*-isomers whereas small coupling constants correlate with a *trans*-configuration of tetraphosphene derivatives. As depicted in Fig. 1, the value of the $^3J_{\text{P}(1)\text{P}(4)}$ constant of $\text{Na}_2[\mathbf{1b}]$ in thf is comparable with that of the contact-ion pair of $\text{Na}_2[\mathbf{1a}]$ which possesses a *s-cis*-configuration.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the triphosphide $\text{Na}[\mathbf{4b}]$ features two signals with the splitting pattern of an AX_2 spin system in the range for the unsaturated two-coordinate phosphorus atoms, as shown in Fig. 2. The chemical shift values for the AX_2 system as well as the large coupling constant ($^1J_{\text{PP}} = 442.0$ Hz) are rather similar to the ^{31}P NMR data recorded for the analogous supersilylated sodium triphosphide $\text{Na}[\mathbf{4a}]$ [43].

The signal pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the sodium pentaphosphide $\text{Na}_2[\mathbf{5b}]$ is comparable with those of the corresponding supersilylated pentaphosphides $\text{M}_2[\mathbf{5a}]$ ($\text{M} = \text{Na}, \text{K}$) [8,10,11]. As indicated in Fig. 3, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Na}_2[\mathbf{5b}]$ shows like that of $\text{Na}_2[\mathbf{5a}]$ three multiplets with the splitting pattern of an $\text{AAB}\ddot{\text{B}}\text{MM}$ spin system. Particularly remarkable are the signals for P(3) and P(4) which are broadened due to Na P coupling. The ^{31}P NMR data of the sodium pentaphosphide $\text{Na}_2[\mathbf{5b}]$ are listed in detail in caption of Fig. 3.

As shown in Fig. 4, the solutions of $\text{Na}_2[\mathbf{1b}]$ and $\text{Na}[\mathbf{4b}]$ have impressing colors. The UV-Vis spectra of $\text{Na}_2[\mathbf{1b}]$ and $\text{Na}[\mathbf{4b}]$ are characterized by absorption bands at $\lambda_{\text{max}} = 491$ nm as well as $\lambda_{\text{max}} = 553$ nm for $\text{Na}_2[\mathbf{1b}]$ and $\lambda_{\text{max}} = 495$ nm as well as $\lambda_{\text{max}} =$

550 nm for $\text{Na}[\mathbf{4b}]$, respectively. The UV-Vis absorption spectra of $\text{Na}_2[\mathbf{1b}]$ and $\text{Na}[\mathbf{4b}]$ resemble each other approximately; the difference is that the spectrum of $\text{Na}[\mathbf{4b}]$ reveals additionally a shoulder at 401 nm (the values of absorption bands of $\text{Na}_2[\mathbf{1b}]$ and $\text{Na}[\mathbf{4b}]$ are mentioned in the caption of Fig. 4). The UV-Vis spectrum of $\text{Na}_2[\mathbf{1a}]$ [7] shows the longest wave absorption band at $\lambda_{\text{max}} = 561$ nm whereas the value of the second band at $\lambda_{\text{max}} = 494$ nm is closely to that at $\lambda_{\text{max}} = 495$ nm in the UV-Vis spectrum of $\text{Na}_2[\mathbf{1b}]$.

DFT calculations reveal that the molecular orbitals (MOs) of the silylated *cis*- and *trans*-tetraphosphene dianions of $[\text{H}_3\text{SiP}=\text{P}=\text{PSiH}_3]^{2-}$, which are comparable with those of the anion in $\text{Na}_2[\mathbf{1b}]$, $[\text{tBu}_2\text{PhSiP}=\text{P}=\text{PSitBu}_3]^{2-}$, show a highest occupied antibonding π^* MO (HOMO). The HOMO is represented by the $(p_z-p_z + p_z-p_z)$ π^* MO with a slight contribution from nonbonding orbitals of the P atoms [7].

X-ray quality crystals of the monophosphanide $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$ were grown from a heptane solution at ambient temperature. The monophosphanide $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$ crystallizes in the monoclinic space group $P2_1/c$ with one complete molecule in the asymmetric unit (Fig. 5; selected bond lengths and angles see caption of Fig. 5). In contrast to alkali metal phosphanediides M_2PSiR_3 , which usually adopt a ladder-type structure the central framework of $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$ is dimeric, forming four-membered rings. This structural motif is also observed for alkali metal chalcogenolates $\text{MESiR}t\text{Bu}_2$ with bulky silyl residues ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{R} = t\text{Bu}, \text{Ph}$) [45–47]. The sodium atoms in $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$ are each coordinated by two P-atoms and two phenyl rings in a distorted tetrahedral fashion, as shown in Fig. 6. The solid structure of $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$ features Na–C contacts between the phenyl rings and the sodium centers with distances ranging from 2.774 to 4.371 Å. In this context it should be noted that the alkali metal centers in the solid-state structures of the silanides $\text{M}[\text{SiPh}t\text{Bu}_2]$ ($\text{M} = \text{Na}, \text{K}$) are coordinated in η^6 -fashion to the phenyl ring of a neighboring silyl group [18,19].

Fig. 3. Observed and calculated ^{31}P NMR spectra of $\text{Na}_2[\mathbf{5b}]$. Chemical shifts and coupling constants [Hz] of $\text{Na}_2[\mathbf{5b}]$: $\delta -88.9$, $\delta -181.6$, $\delta -242.8$, $^1J_{\text{P}(1/3)\text{P}(1/3)} = -193.7$, $^1J_{\text{P}(1/3)\text{P}(2)} = -187.7$, $^2J_{\text{P}(1/3)\text{P}(4/5)} = -6.3$, $^2J_{\text{P}(2)\text{P}(4/5)} = 69.5$, $^1J_{\text{P}(4/5)\text{P}(1/3)} = -335.2$, $^3J_{\text{P}(4/5)\text{P}(4/5)} = 222.6$.

Fig. 4. UV-Vis absorbance spectra of $\text{Na}_2[\mathbf{1b}]$ (red solution; red curve) and $\text{Na}[\mathbf{4b}]$ (purple solution; blue dashed curve) in thf. $\text{Na}_2[\mathbf{1b}]$: $\lambda_{\text{max}} = 553 \text{ nm}, 491 \text{ nm}$; $\text{Na}[\mathbf{4b}]$: $\lambda_{\text{max}} = 550 \text{ nm}, 495 \text{ nm}$; $\text{Na}_2[\mathbf{1a}]$: $\lambda_{\text{max}} = 561 \text{ nm}, 494 \text{ nm}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Structure of $\{\text{Na}[\text{P}(\text{SiPhtBu}_2)_2]\}_2$ in the crystal; displacement ellipsoids are drawn at the 50% probability level. Selected structural parameters (lengths (Å) and angles ($^\circ$)): $\text{P}(1)\text{--Si}(1)$ 2.2348(17), $\text{P}(1)\text{--Si}(2)$ 2.235(2), $\text{P}(1)\text{--Na}(2)$ 2.887(3), $\text{P}(1)\text{--Na}(1)$ 2.897(3), $\text{Na}(1)\text{--P}(1)\#1$ 2.897(3), $\text{Na}(1)\text{--Na}(2)$ 3.291(5), $\text{Na}(2)\text{--P}(1)\#1$ 2.887(3), $\text{Si}(1)\text{--C}(11)$ 1.915(6), $\text{Si}(1)\text{--C}(17)$ 1.940(6), $\text{Si}(1)\text{--C}(18)$ 1.942(6), $\text{Si}(2)\text{--C}(21)$ 1.923(6), $\text{Si}(2)\text{--C}(28)$ 1.929(6), $\text{Si}(2)\text{--C}(27)$ 1.959(6), $\text{Si}(1)\text{--P}(1)\text{--Si}(2)$ 129.89(9), $\text{Si}(1)\text{--P}(1)\text{--Na}(2)$ 98.44(8), $\text{Si}(2)\text{--P}(1)\text{--Na}(2)$ 126.11(6), $\text{Si}(1)\text{--P}(1)\text{--Na}(1)$ 115.92(7), $\text{Si}(2)\text{--P}(1)\text{--Na}(1)$ 101.83(8), $\text{Na}(2)\text{--P}(1)\text{--Na}(1)$ 69.35(9), $\text{P}(1)\#1\text{--Na}(1)\text{--P}(1)$ 110.38(14), $\text{P}(1)\#1\text{--Na}(1)\text{--Na}(2)$ 55.19(7), $\text{P}(1)\text{--Na}(1)\text{--Na}(2)$ 55.19(7), $\text{P}(1)\#1\text{--Na}(2)\text{--P}(1)$ 110.93(14), $\text{P}(1)\#1\text{--Na}(2)\text{--Na}(1)$ 55.46(7), $\text{P}(1)\text{--Na}(2)\text{--Na}(1)$ 55.46(7). Symmetry transformation used to generate equivalent atoms: $\#1 -x + 1, y, -z + 3/2$.

There are only a few other crystallographically characterized unsupported disilylated alkali metal monophosphanides which have been reported in the literature [48–55]. The Si–P bonds in $\{\text{Na}[\text{P}(\text{SiPhtBu}_2)_2]\}_2$ are longer than the corresponding bonds in

the triphenylsilyl species $\{\text{Li}[\text{P}(\text{SiPh}_3)_2]\}_2$ [48] (averaged Si–P bond lengths: 2.235(2) Å ($\{\text{Na}[\text{P}(\text{SiPhtBu}_2)_2]\}_2$) versus 2.187(2) Å ($\{\text{Li}[\text{P}(\text{SiPh}_3)_2]\}_2$)).

Fig. 6. Crystal packing diagram of $\{\text{Na}[\text{P}(\text{SiPh}t\text{Bu}_2)_2]\}_2$.

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