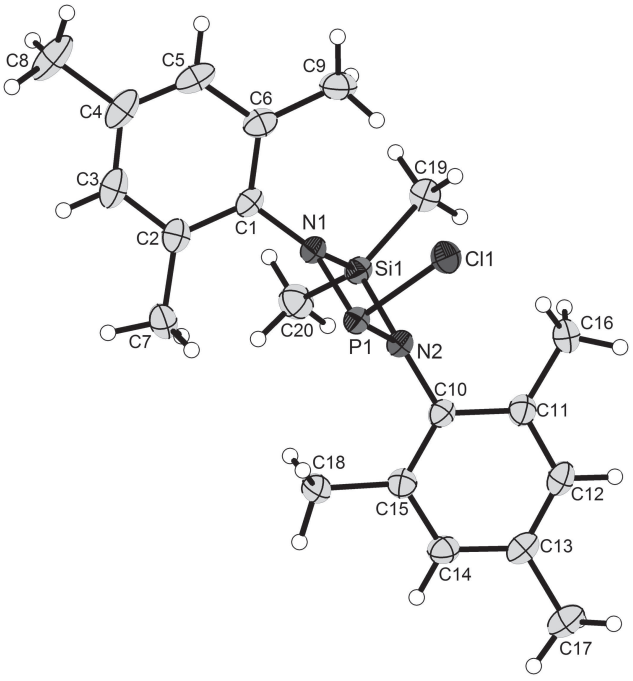
Open Access

Verena Breuers and Walter Frank*

The crystal structure of 2-chloro-1,3-bis(2,4,6-trimethylphenyl)-4,4-dimethyl-1,3,2λ^3,4-diazaphosphasiletidine



DOI 10.1515/ncrs-2015-0176
Received August 5, 2015; accepted January 18, 2016; available online February 16, 2016

Abstract

$C_{20}H_{28}ClN_2PSi$, orthorhombic, *Pbca* (no. 61), $a = 16.811(3)$ Å, $b = 14.357(3)$ Å, $c = 17.523(3)$ Å, $V = 4229.3(14)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0429$, $wR_{ref}(F^2) = 0.1233$, $T = 123(2)$ K.

CCDC no.: 1447972

***Corresponding author: Walter Frank,** Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Material- und Strukturforschung, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany, e-mail: wfrank@uni-duesseldorf.de

Verena Breuers: Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Material- und Strukturforschung, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Table 1: Data collection and handling.

Crystal:	Yellow plate, size 0.1×0.2×0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.34 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ-scans
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	52947, 3691
$N(param)_{refined}$:	244
Programs:	SHELX [6], DIAMOND [7]

Table 2: Fractional atomic coordinates and isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	8*c*	0.3495	0.4442	−0.2641	0.043
H(5)	8*c*	0.5346	0.3960	−0.1245	0.044
H(7A)	8*c*	0.2011	0.3694	−0.1537	0.057
H(7B)	8*c*	0.2185	0.4380	−0.2238	0.057
H(7C)	8*c*	0.2065	0.4794	−0.1397	0.057
H(8A)	8*c*	0.4844	0.4655	−0.3111	0.082
H(8B)	8*c*	0.5141	0.3618	−0.2935	0.082
H(8C)	8*c*	0.5584	0.4488	−0.2553	0.082
H(9A)	8*c*	0.4317	0.4051	0.0469	0.055
H(9B)	8*c*	0.5180	0.3927	0.0098	0.055
H(9C)	8*c*	0.4604	0.3046	0.0185	0.055
H(12)	8*c*	0.0359	0.3185	0.2695	0.038
H(14)	8*c*	−0.0785	0.3678	0.0721	0.035
H(16A)	8*c*	0.1764	0.3410	0.2791	0.058
H(16B)	8*c*	0.2276	0.3669	0.2051	0.058
H(16C)	8*c*	0.2044	0.2607	0.2217	0.058
H(17A)	8*c*	−0.1103	0.3658	0.2663	0.060
H(17B)	8*c*	−0.1238	0.2662	0.2274	0.060
H(17C)	8*c*	−0.1546	0.3585	0.1856	0.060
H(18A)	8*c*	−0.0135	0.3934	−0.0416	0.049
H(18B)	8*c*	0.0665	0.3341	−0.0509	0.049
H(18C)	8*c*	0.0711	0.4436	−0.0343	0.049
H(19A)[a]	8*c*	0.3565	0.1814	0.0557	0.045
H(19B)[a]	8*c*	0.2865	0.1752	0.1173	0.045
H(19C)[a]	8*c*	0.3453	0.2629	0.1171	0.045
H(20A)	8*c*	0.2449	0.1603	−0.0733	0.058
H(20B)	8*c*	0.1713	0.2299	−0.0835	0.058
H(20C)	8*c*	0.1698	0.1529	−0.0175	0.058

[a]Occupancy factor: 0.879.

Table 3: Fractional atomic coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	8*c*	0.30486(3)	0.50678(4)	0.11579(3)	0.0326(3)	0.0357(3)	0.0294(3)	−0.0022(2)	−0.0030(2)	−0.0059(2)
P(1)	8*c*	0.23021(3)	0.45448(4)	0.02343(3)	0.0233(3)	0.0270(3)	0.0229(3)	0.0010(2)	0.0018(2)	0.0015(2)
Si(1)	8*c*	0.25084(3)	0.27853(4)	0.01935(3)	0.0221(3)	0.0259(3)	0.0253(3)	−0.0011(2)	0.0024(2)	−0.0006(2)
N(1)	8*c*	0.2916(1)	0.3789(1)	−0.02070(9)	0.0231(8)	0.0274(9)	0.0216(8)	−0.0011(6)	0.0026(6)	0.0016(6)
N(2)	8*c*	0.18743(9)	0.3594(1)	0.06205(9)	0.0226(8)	0.0282(9)	0.0224(8)	−0.0003(6)	0.0019(6)	0.0010(7)
C(1)	8*c*	0.3460(1)	0.3973(1)	−0.0820(1)	0.0247(9)	0.024(1)	0.0258(9)	−0.0031(8)	0.0059(8)	−0.0020(8)
C(2)	8*c*	0.3161(1)	0.4184(2)	−0.1547(1)	0.035(1)	0.028(1)	0.027(1)	−0.0026(8)	0.0029(8)	0.0002(8)
C(3)	8*c*	0.3694(1)	0.4294(2)	−0.2148(1)	0.049(1)	0.032(1)	0.027(1)	−0.004(1)	0.0102(9)	0.0019(9)
C(4)	8*c*	0.4507(1)	0.4194(2)	−0.2046(1)	0.047(1)	0.027(1)	0.039(1)	−0.0054(9)	0.019(1)	−0.0018(9)
C(5)	8*c*	0.4788(1)	0.4014(2)	−0.1321(1)	0.028(1)	0.031(1)	0.050(1)	−0.0039(9)	0.0135(9)	−0.004(1)
C(6)	8*c*	0.4284(1)	0.3910(1)	−0.0695(1)	0.027(1)	0.026(1)	0.036(1)	−0.0023(8)	0.0037(8)	−0.0032(8)
C(7)	8*c*	0.2278(1)	0.4271(2)	−0.1693(1)	0.039(1)	0.050(2)	0.026(1)	−0.001(1)	−0.0044(9)	0.007(1)
C(8)	8*c*	0.5069(2)	0.4243(2)	−0.2721(2)	0.065(2)	0.043(2)	0.056(2)	−0.002(1)	0.038(1)	0.003(1)
C(9)	8*c*	0.4626(1)	0.3716(2)	0.0082(1)	0.023(1)	0.043(1)	0.044(1)	0.0005(9)	−0.0020(9)	−0.003(1)
C(10)	8*c*	0.1126(1)	0.3550(1)	0.1013(1)	0.0231(9)	0.026(1)	0.0240(9)	−0.0016(7)	0.0031(7)	0.0000(8)
C(11)	8*c*	0.1111(1)	0.3375(2)	0.1803(1)	0.031(1)	0.031(1)	0.024(1)	−0.0013(8)	0.0023(8)	0.0015(8)
C(12)	8*c*	0.0374(1)	0.3307(2)	0.2162(1)	0.036(1)	0.034(1)	0.025(1)	−0.0014(9)	0.0072(8)	0.0037(8)
C(13)	8*c*	−0.0335(1)	0.3409(2)	0.1773(1)	0.030(1)	0.028(1)	0.034(1)	−0.0024(8)	0.0090(8)	−0.0019(9)
C(14)	8*c*	−0.0303(1)	0.3597(2)	0.0995(1)	0.023(1)	0.032(1)	0.033(1)	−0.0028(8)	0.0005(8)	−0.0015(8)
C(15)	8*c*	0.0418(1)	0.3671(1)	0.0607(1)	0.027(1)	0.027(1)	0.026(1)	−0.0027(8)	0.0005(8)	−0.0005(8)
C(16)	8*c*	0.1865(1)	0.3255(2)	0.2255(1)	0.036(1)	0.055(2)	0.024(1)	0.003(1)	−0.0012(8)	0.007(1)
C(17)	8*c*	−0.1125(1)	0.3321(2)	0.2177(1)	0.033(1)	0.044(1)	0.043(1)	−0.002(1)	0.014(1)	0.002(1)
C(18)	8*c*	0.0414(1)	0.3862(2)	−0.0239(1)	0.026(1)	0.045(1)	0.028(1)	−0.0034(9)	−0.0024(8)	0.0033(9)
C(19)[a]	8*c*	0.3176(6)	0.2174(6)	0.0850(5)	0.035(4)	0.024(4)	0.030(3)	0.001(3)	0.002(2)	0.001(2)
Cl(1A)[b]	8*c*	0.322(1)	0.213(2)	0.089(1)	0.041(8)	0.05(1)	0.052(9)	0.014(6)	−0.015(6)	0.017(6)
C(20)	8*c*	0.2037(1)	0.1958(2)	−0.0464(1)	0.039(1)	0.038(1)	0.038(1)	−0.000(1)	−0.0034(9)	−0.003(1)

[a]Occupancy factor: 0.879; [b]Occupancy factor: 0.121.

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared according to common procedures under argon atmosphere in oven-dried glassware using Schlenk techniques [1–5]. In a typical reaction, 1.3 g (3.9 mmol) *N*,*N*′-bis(2,4,6-trimethylphenyl)-*Si*,*Si*-dimethylsilanediamine were dissolved in 20 mL *n*-pentane. After cooling to −10 °C 5 mL *n*-butyllithium (1.6 mol·l^{-1} in hexane, 8 mmol) were added. Afterwards the reaction mixture was stirred for 12 h at room temperature. Cooling to −20 °C and addition of 0.6 g (4.0 mmol) PCl_3 yielded a yellow suspension. After filtration and removal of the solvent under reduced pressure the crude product was obtained as viscous oil. Plate-shaped yellow crystals result from repeated recrystallization from toluene. The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} **NMR spectra** were recorded with a Bruker Avance III 400 spectrometer using sealed J-Young NMR tubes. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 0.56 (s, 3H, $SiCH_3$), 0.82 (s, 3H, $SiCH_3$), 2.28 (s, 6H, *p*-Me), 2.51 (s, 12H, *o*-Me), 6.92 (s, 4H, Ar—H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 25 °C): δ (ppm) 3.0 (s, $SiCH_3$), 8.1 (s, $SiCH_3$), 20.0 (d, ^4J(P,C) = 4.9 Hz, 4C; *o*-CH_3), 20.0 (s, *p*-CH_3), 129.6 (s, Ar—C—H), 134.4 (s, *o*-C—CH_3), 135.4 (s, *p*-C—CH_3), 136.6 (s, Ar—C—N). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 25 °C): δ (ppm) 210.0 (s). EI-MS spectra were obtained using a Finnigan TSQ 7000 instrument. EI-MS: m/z (%) 390 (4) [M^+], 164 (49) [MesNP], 135 (100) [$MesNH_2$], 120 (61) [Mes]. IR spectroscopic data were measured using a Bio-Rad Excalibur FTS 3500 FT-IR spectrometer with ATR-unit, 4000–560 cm^{-1}: 2957(*s*), 2920(*s*), 2858(*m*), 1607(*w*), 1524(*w*), 1475(*s*), 1378(*w*), 1307(*w*), 1258(*s*), 1236(*s*), 1221(*s*), 1201(*m*), 1147(*m*), 1077(*s*), 963(*m*), 893(v), 875(*s*), 810(*s*), 793(*s*).

Experimental details

All hydrogen atoms were identified via difference Fourier synthesis and the riding model was applied using idealized positions. In addition, the H atoms of the CH_3 groups were allowed to rotate around the neighboring C—C bonds. Their U_{iso} values were set to $1.5U_{eq}(C_{methyl})$ and $1.2U_{eq}(C_{ar})$, respectively. To account for high residual electron density in the coordination sphere of the Si atom and a difference of the Si—C bond lengths that does not appear to be physically meaningful,

a partial occupation site model has been introduced with a Cl/Me ratio of 12.1(4)%/87.9(4)%.

Discussion

Bis(amino)silanes $R_2Si(NHR')_2$ are known as attractive synthetic building blocks in heterocyclic chemistry. Their synthesis was first described more than 50 years ago [1] while their reaction and coordination behavior has been extensively studied during the following years [2–5, 8–12]. Particularly diazaphosphasiletidines resulting from this versatile silylamine precursors have attracted considerable attention in phosphorus chemistry [2–5]. The title compound is the first structurally characterized chloro substituted diazaphosphasiletidine.

The asymmetric unit of the crystal structure of the title compound contains one molecule and is dominated by its central and almost planar SiN_2P four-membered ring. Within the ring the nitrogen atoms exhibit a trigonal planar coordination sphere (bond angle sums 358.82° (N1) and 358.53° (N2)) whereas the phosphorus and the silicon atom bear the main ring strain (angles N1—Si1—N2 82.14(8)° and N1—P1—N2 85.65(8)°). The geometrical parameters of the N—Si—N fragment further serve as probe for the electronic interactions within the ring system [5]. The unusually acute N1—Si1—N2 angle in the title compound is associated with Si—N distances of 1.7436(17) Å (Si1—N1) and 1.7445(17) Å (Si1—N2). The latter are remarkably longer than the value reported for a Si—N single bond (1.724(4) Å [13]), but correspond to those in related cyclodisilazanes [14–22]. Consequently, the P—N bonds are shorter than expected for a single bond (1.6857(17) Å (P1—N1) and 1.6854(17) Å (P1—N2) vs. 1.704(4) Å [13]). Competing with the silicon atom for the nitrogen lone pairs, the phosphorus apparently is the stronger interaction partner. This concept also explains the elongation of the P—Cl bond (2.1813(7) Å) compared with the P—Cl distance in PCl_3 (2.034 Å) [23]. However, additional steric factors should not be neglected: The mesityl substituents do not take a coplanar position with respect to the SiN_2P ring, but form angles of 75.64(6)° and 77.16(6)°, respectively. For similar diazadiphosphetidines $[ClPNR]_2$ angles between 0° and 90° have been found depending on the steric requirements of the aryl substituents [24–27]. Considering the Si—N and P—N bond lengths as well as the absence of any residual electron density at the phosphorus atom opposite to the Cl atom position, there is no disorder model to account for the partial occupation site near Si1. We therefore have to assume that the crystal of the title compound under investigation contains approximately 12% of a second compound, namely 2-chloro-1,3-bis(2,4,6-trimethylphenyl)-4-chloro-4-methyl-1,3,2λ^3,4-diazaphosphasiletidine exhibiting a Si1—Cl distance of 2.015 Å. A comparison of the solid state packings of the title compound and of the higher congeners of group 15 gives useful insights: Despite some structural differences the El—Cl distances in all compounds are larger than the sum of the covalence radii [28]. Furthermore, the association of the molecules via El—Cl bridging bonds increases from P to Bi [29, 30]. Whereas the title compound consists of isolated molecules, $Me_2Si(N^tBu)_2AsCl$ contains dimers and in the antimony and bismuth compounds the molecules are connected via bridging Cl atoms to form one-dimensional chains.

Acknowledgements: We thank the Fonds der Chemischen Industrie for support and E. Hammes and P. Roloff for technical support.

References

1. Fink, W.: Beiträge zur Chemie der Si-N-Bindung, II. Zur Kenntnis von *N.N'*-Bis-trimethylsilyl-tetramethylcyclodisilazan und anderen 4 gliedrigen Silicium und Stickstoff enthaltenden Ringen. Chem. Ber. **96** (1963) 1071–1079.
2. Neemann, J.; Klingebiel, U.: Reaktionen von Lithioaminofluorsilanen mit kovalenten Elementhalogeniden. Chem. Ber. **114** (1981) 527–535.
3. Scherer, O. J.; Püttmann, M.; Krüger, C.; Wolmershäuser, G.: Elementorganische Amin/Imin-Verbindungen, XXIII. Aminophosphan- und Aminophosphoran-Rotamere. Chem. Ber. **115** (1982) 2076–2124.
4. Eichhorn, B.; Nöth, H.: New diazasila phosphetidines and their precursors. Z. Naturforsch. **55b** (2000) 352–360.
5. Veith, M.; Bertsch, B.; Huch, V.: Zur Element-Stickstoff-Doppelbindung in Kationen cyclischer Bis(amino)-phospha-, -arsa-, -stiba- und -bismutane. Z. Anorg. Allg. Chem. **559** (1988) 73–88.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
7. Brandenburg, K.: DIAMOND, Crystal Impact GbR, Bonn, Germany, 2012.
8. Veith, M.: Cyclic nitrogen derivatives of tetra- and divalent tin. Angew. Chem. Int. Ed. **14** (1975) 263–264.
9. Veith, M.; Frank, W.; Töllner, F.; Lange, H.: Stickstoffverbindungen von Elementen der dritten Hauptgruppe mit intra- und intermolekularen Donor-Akzeptor-Bindungen: IV. Polycyclische Alumina-, Lithia-, Magnesia- und Sodia-silazane. J. Organomet. Chem. **326** (1987) 315–333.
10. Passarelli, V.; Benetollo, F.; Zanella, P.; Carta, G.; Rossetto, G.: Synthesis and characterisation of novel zirconium(IV) derivatives containing the bis-amido ligand $SiMe_2(NRR')_2$. Dalton Trans. (2003) 1411–1418.
11. Breuers, V.; Lehmann, C. W.; Frank, W.: Unusual bonding and properties in main group element chemistry: rational synthesis, characterization, and experimental electron density determination of mixed-valent tetraphosphetes. Chem. Eur. J. **21** (2015) 4596–4606.
12. Frank, W.; Petry, V.; Gerwalin, E.; Reiss, G. J.: Synthesis, structure, and bonding of a mixed-valent tetraphosphete. Angew. Chem. Int. Ed. **35** (1996) 1512–1514.
13. Brown, I. D.; Altermatt, D.: Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Crystallogr. **B41** (1985) 244–247.

14. Párkányi, L.; Argay, G.; Hencsei, P.; Nagy, J.: Crystal and molecular structure of tetramethyl-*N*,*N*′-diphenylcyclodisilazane. J. Organomet. Chem. **116** (1976) 299–305.
15. Clegg, W.; Klingebiel, U.; Sheldrick, G. M.; Vater, N.: Darstellung und Molekülstruktur von 1,3-Diaza-2,4-disilacyclobutanen. Z. Anorg. Allg. Chem. **482** (1981) 88–94.
16. Bihátsi, L.; Hencsei, P.; Párkányi, L.: The structure of tetramethyl-*N*,*N*′-bis-*o*-tolylcyclodisilazane. J. Organomet. Chem. **219** (1981) 145–151.
17. Szöllösy, Á.; Párkányi, L.; Bihátsi, L.; Hencsei, P.: Conformational study of tetramethyl-*N*,*N*′-bis-arylcyclodisilazanes by ^{13}C NMR and X-ray diffraction methods. J. Organomet. Chem. **251** (1983) 159–166.
18. Clegg, W.; Haase, M.; Sheldrick, G. M.; Vater, N.: Structure of 1,3-di-*tert*-butyl-2,2,4,4-tetraisopropylcyclodisilazane, $C_{20}H_{46}N_2Si_2$. Acta Crystallogr. **C40** (1984) 871–873.
19. Shah, S. A. A.; Roesky, H. W.; Lubini, P.; Schmidt, H.-G.: 1,3-Bis(2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-1,3-diaza-2,4-disilacyclobutane. Acta Crystallogr. **C52** (1996) 2810–2811.
20. Schneider, J.; Popowski, E.; Junge, K.; Reinke, H.: Reaktionen von Lithiumhydridosilylamiden RR′(H)Si—N(Li)R″ mit Chlortrimethylsilan in Tetrahydrofuran und unpolaren Lösungsmitteln: N-Silylierung und/oder Cyclodisilazanbildung. Z. Anorg. Allg. Chem. **627** (2001) 2680–2692.
21. Kocher, N.; Selinka, C.; Leusser, D.; Kost, D.; Kalikhman, I.; Stalke, D.: Experimental charge density studies of cyclotetrasilazane and metal complexes containing the di- and tetraanion. Z. Anorg. Allg. Chem. **630** (2004) 1777–1793.
22. Anagho, L. E.; Bickley, J. F.; Steiner, A.; Stahl, L.: Synthesis and solid-state structure of a metal complex of a diphosphineimine. Angew. Chem. Int. Ed. **44** (2005) 3271–3275.
23. Galy, J.; Enjalbert, R.: Crystal chemistry of the VA element trihalides: lone pair, stereochemistry, and structural relationships. J. Solid State Chem. **44** (1982) 1–23.
24. Bashall, A.; Doyle, E. L.; García, F.; Lawson, G. T.; Linton, D. J.; Moncrieff, D.; McPartlin, M.; Woods, A. D.; Wright, D. S.: Suggestion of a “twist" mechanism in the oligomerisation of a dimeric phospha(III)zane: insights into the selection of adamantoid and macrocyclic alternatives. Chem. Eur. J. **8** (2002) 5723–5731.
25. Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P.: Synthesis and structural characterization of manganese(II) derivatives of the bulky, chelating bis(amido) ligands $[(NMes)_2SiMe_2]^{2-}$ and $[DippNCH_2CH_2NDipp]^{2-}$, their neutral amine precursors, and their lithium salts (Mes = 2,4,6-$Me_3C_6H_2$; Dipp = 2,6-*i*-$Pr_2C_6H_3$). Inorg. Chem. **30** (1991) 2487–2494.
26. Ahlemann, J.-T.; Roesky, H. W.; Murugavel, R.; Parisini, E.; Noltemeyer. M.; Schmidt, H.-G.; Müller, O.; Herbst-Irmer, R.; Markovskii, L. N.; Shermilovich, Y. G.: The role of the 2,4,6-tris(trifluoromethyl)phenylamino group in stabilizing new phosphorus-, arsenic-, and germanium-containing main-group compounds and transition-metal derivatives. Chem. Ber. **130** (1997) 1113–1121.
27. Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E.: Transformations between monomeric, dimeric, and trimeric phosphazanes: oligomerizing NP analogues of olefins. J. Am. Chem. Soc. **124** (2002) 14012–14013.
28. Hollemann, A. F.; Wiberg, E.; Wiberg, N.: *Lehrbuch der Anorganischen Chemie*, 102th ed., de Gruyter, Berlin [u.a.], **2007**.
29. Veith, M.; Bertsch, B.: Cyclische Bis(amino)-arsa-, -stiba-, bismachloride und ein spezielles Tris(amino)bismutan. Z. Anorg. Allg. Chem. **557** (1988) 7–122.
30. Ma, X.; Ding, Y.; Roesky, H. W.; Sun, S.; Yang, Z.: Synthesis and crystal structures of antimony(III) complexes with a bis(amino)silane ligand. Z. Anorg. Allg. Chem. **639** (2013) 49–52.