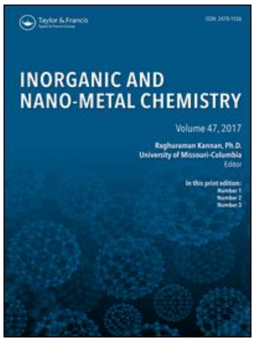

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Synthesis and X-ray crystal structure of novel tetramethylphosphonium dichlorodimethylaluminate

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ABSTRACT

The reaction of tris(trimethylsilyl)phosphine with dimethylaluminum chloride in 1,2-dimethoxyethane (monoglyme) displays an important role as building blocks that results in the production of novel tetramethyl phosphonium dichlorodimethylaluminate and the already known dimer compound (bis(2,2-methoxy-ethanolato-O,O′)-tetramethyl-di-aluminum). The newly formed tetramethyl phosphonium dichlorodimethylaluminate $[(CH_3)_4P]^+[(CH_3)_2AlCl_2]^-$ crystallizes in the monoclinic space group $P2_1/c$, having unit cell with lattice constants $a = 7.522$, $b = 11.644$, $c = 14.841$ Å, and $\beta = 99.32°$ includes four formula units. The mean values of the bond lengths are P-C 1.787 Å, Al-Cl 2.224 Å, and Al-C 1.966 Å. Both phosphorus and aluminum are tetrahedrally surrounded in organophosphonium-based cations and organoaluminium-based anions. The geometry of the dichlorodimethylaluminate anion shows a distorted tetrahedron.

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Phosphine; phosphonium; aluminate; monoglyme; crystal structure

Introduction

It is known that the common synthetic methods for the preparation of quaternary phosphonium cations have been produced by the addition of alkyl- or aryl-halides to the appropriate phosphines.[1–6] Most tetraalkylphosphonium salts are prepared by alkylation of tertiary phosphines with appropriate alkyl halides.[1–5] On the other hand, most tetraarylphosphonium salts are generated by the complex salt method. In this case, aryl halides have been heated with appropriate tertiary phosphines in the presence of nickel complex as catalysis.[6] Quaternary phosphonium salts can be considered as Lewis acid organocatalysts. The catalytic applications of these phosphonium salts are phase-transfer catalysis in organic reactions.[7] Tris(trimethylsilyl)phosphine compound, commonly known as a starting material,[8] is probably the most important compound of phosphorus chemistry with various applications in the main-groups,[9–13] transition metal chemistry,[14,15] and organic synthesis.[16,17] As known so far, the reaction of tris(trimethylsilyl)phosphine with organic electrophiles via cleavage of the weak polar Si-P bonds, leads to different classes of starting materials.[8] $1\lambda^3$-phosphaalkenes[18,19] and $1\lambda^3$-phosphaalkynes,[19–26] prepared from tris(trimethylsilyl)phosphine, have high reactivity in the field of organoelements and organometallic chemistry. In this context, synthesis and structural study of new tris(trimethylsilyl)phosphine derivatives are an important area in the molecular chemistry. Consequently, main-group elements and transition metal phosphines complexes are ubiquitous and indispensable in research areas such as homogeneous catalysis and organic synthesis, etc.[8–26] Recently, the combined insertion of phosphaalkyne and oligomerization reactions of the elements group 13 and 15 have found renewed interest.[22–26] Besides, unusual phosphorus oligocycle structures have been prepared and studied. Lewis acid-base adducts of the elements group 13 and 15 have been synthesized and structurally characterized, due to their importance in chemical synthesis.[13,14,27] In contrast, the reactions of methylaluminium dichloride or aluminum trichloride with diglyme have been studied, which explore the cleavage of diglyme to provide an Al-O bond in the synthesized compound via methyl chloride elimination.[28] Lehmkuhl et al. examined the stability of these adducts and investigated reactions of aluminum derivatives with diglyme which lead partly to the formation of the unexpected diglyme cleavages. The dimer aluminum alkoxide compound has also been prepared via diglyme cleavages by using dimethyl alane.[28] As a consequence, this prompted an investigation of the final product by elemental analysis,[28] NMR spectroscopy,[28–31] and X-ray structure analysis.[30,32] Recently, a series of tricyclic phosphonium salts[22] is derived from the diorganophosphorus halides and 2-*tert*-butyl-$1\lambda^3$-phosphaalkyne, which shows substantial interest. The quantum chemical calculation was applied to these phosphonium salts, which can be regarded as a conventional trigonal bipyramid structure, that would afford interest in future research. Moreover, different studies of high-quality phosphonium salt materials showed strong antimicrobial, antibacterial, and antifungal activities.[33–36]

Furthermore, the environment-friendly and the relatively low toxicity of phosphonium salts have been reported by

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similar studies.[37,38] Owing to the need for more environment-friendly, this work is carried out on phosphonium aluminate salts. The present article has focused on the reactions of tris(trimethylsilyl)phosphine with organoaluminium halides in 1,2-dimethoxyethane (monoglyme), that show important role as building blocks in phosphonium dialkyldihaloaluminate chemistry, followed by the characterization of $[(CH_3)_4P]^+[(CH_3)_2AlCl_2]^-$ the type of compounds.

Experimental section

General procedures characterization

All manipulations of air- and moisture-sensitive materials were performed with the exclusion of oxygen and moisture by applying standard Schlenk techniques under an atmosphere of argon (purity >99.998%), which was freed from oxygen with BTS catalyst[39] and dried with P_4O_{10}. All of the reagents and common solvents were purchased from Merck, Sigma-Aldrich Co. in 95 – 99.5% purity or synthesized according to published procedures. The common solvents (1,2-dimethoxyethane, *n*-hexane, benzene, and toluene) were dried over NaK/benzophenone and distilled under argon before use.[22–24] Dimethylaluminium chloride was purchased from Merck Sigma-Aldrich Co. (packaged under nitrogen in poly-coated Sure/Seal^{TM} bottles) as 1 M solution in *n*-hexane.

Instruments and measurements

NMR spectra were recorded on Bruker AM 200, AC 250, and AM 400 MHz spectrometers, chemical shifts were referenced to internal solvent resonances and are reported relative to TMS for ^1H and $^{13}C\{^1H\}$ chemical shifts and to the external 85% aqueous solution of H_3PO_4 for $^{31}P\{^1H\}$ chemical shifts as well as acetylacetonatoaluminium(III), saturated solution in C_6D_6 for $^{27}Al\{^1H\}$ chemical shifts. All NMR samples were prepared in 5 or 10 mm tubes which were flame-sealed under argon. All the NMR measurements were obtained at room temperature unless otherwise stated. Elementary analyses were carried out using a Perkin-Elmer Series II Analyzer 2400. Melting points (uncorrected) were determined using a Büchi apparatus, with samples sealed in capillaries under argon. Single crystals were separated directly from the solution at room temperature under argon and covered with polyfluorinated polyether oil (RS 3000, Riedel-de-Haën) and then the crystals are cooled down to $-100 \pm 3\,°C$ in a stream of nitrogen.[40] Reflections were obtained using a Siemens P3 (Syntex P21) four-circle diffractometer with Mo Kα radiation and a graphite monochromator. Structures were solved by direct methods and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 with the programs SHELXTL Plus (data reduction), SHELXS (structure solving), and SHELXL (structure refinement).[41,42] The hydrogen atoms of **2** and **3** were added in calculated positions, included in the final stage of refinement, and allowed to ride on their respective carbon atoms.

Preparation of tris(trimethylsilyl)phosphine ($(Me_3Si)_3P$)

Tris(trimethylsilyl)phosphine was prepared according to literature methods.[8,22–24] Sodium/potassium alloy reacts with white and red phosphorus in 1,2-dimethoxyethane followed by the addition of a slight excess of freshly distilled chlorotrimethylsilane. Finally, the solvent was distilled off at atmospheric pressure, and the remaining tris(trimethylsilyl)phosphine was purified by vacuum distillation.

$$NMR^{31}P\{^1H\} : \delta = \ -251.50 \text{ ppm (s); solution in } d_6 - \text{benzene}$$

Preparation of $[((CH_3)_3Si)_3P{\bullet}Al(CH_3)_2Cl]$ (1)

A solution of dimethylaluminum chloride in *n*-hexane (5 mmol) was added to a stirred solution of *tris*(trimethylsilyl)phosphine (5 mmol) in *n*-hexane (15 mL) over a period of 2 h at −78 °C. When the reaction mixture was allowed to warm up to the room temperature, stirring was continued for 12 h. The solution slowly turned yellow, and a colorless solid precipitated ($[((CH_3)_3Si)_3P{\bullet}Al(CH_3)_2Cl]$) (**1**). Inside the drybox, the solvent was decanted from the solid. An evaporation of the residual solvent from the solid resulted in **1** (1.5251 g, 88.9% yield), mp 171 °C. X-ray quality crystals were unobtainable. Anal. Calc. (Found) for $C_{11}H_{33}A1C1PSi_3$: C, 38.51 (38.29); H, 9.70 (9.74); C1, 10.33 (10.21); P, 9.03 (8.97). ^1H NMR: $\delta =$ – 0.59 ppm (br,s, $AlC\mathbf{H}_3$, 6 H), 0.21 ppm [d, $Si(C\mathbf{H}_3)_3$, 27 H, $^3J_{HP} = 4.21$ Hz]. $^{13}C\{^1H\}$ NMR: $\delta =$ – 8.5 ppm (**s,** $Al\mathbf{C}H_3$), 3.1 ppm [d, $Si(\mathbf{C}H_3)_{3,}$ $^2J_{CP} = 11.21$]. $^{27}Al\{^1H\}$ NMR: $\delta =$ 160.0 ppm (br,s, $W_{1/2} = 2050$ Hz). $^{31}P\{^1H\}$ NMR: $\delta =$ – 246.77 ppm (s); solution in d_6-benzene.

Preparation of tetramethyl phosphonium dichlorodimethylaluminate ($[Me_4P]^+[Me_2AlCl_2]^-$) (2) and bis(2,2-methoxy-ethanolato-O,O′)-tetramethyl-di-aluminum $[Me_2AlO(CH_2)_2OMe]_2$ (3)

A solution of dimethylaluminum chloride in *n*-hexane (10 mmol) was added to a stirred solution of *tris*(trimethylsilyl)phosphine (10 mmol) in *n*-hexane (25 mL) for 2 h at −78 °C. When the reaction mixture was allowed to warm up to room temperature, stirring was continued for 12 h. The solution slowly turned yellow, and a colorless solid precipitated. Solvent and any excess of dimethylaluminum chloride were removed without filtration very slowly under reduced pressure. The residue was washed with cold *n*-hexane and dissolved in 1,2-dimethoxyethane (25 mL), then stirring was continued for 12 h at room temperature. The solution was kept overnight at room temperature, and the colorless plate crystals (0.50 × 0.40 × 0.20) were filtered at room temperature ($C_{10}H_{26}Al_2O_4$) (**2**). The filtrate in 1,2-dimethoxyethane was kept cold at – 60 °C for 1 week, and the colorless block crystals (0.50 × 0.50 × 0.30) were obtained ($[Me_4P]^+[Me_2AlCl_2]^-$) (**3**).

2 (1.1 g, 41.6% yield), mp 120 °C. X-ray quality crystals were obtainable. Anal. Calc. (Found) for $C_{10}H_{26}A_{12}O_4$: C, 45.45 (45.30); H, 9.92 (9.71). ^1H NMR: $\delta =$ – 0.71 ppm (br,s, Al-C$\mathbf{H}_3$, 12 H), 2.50 ppm (br,s, O-C$\mathbf{H}_3$, 6 H), 2.88 ppm (br,s, CH_3-O-C$\mathbf{H}_2$, 4 H), 3.34 ppm (br,s, O-C$\mathbf{H}_2$, 4 H). $^{13}C\{^1H\}$ NMR: $\delta = -10.9$ ppm (s, Al$\mathbf{C}H_3$), 57.0 (s, CH_3-O-$\mathbf{C}H_2$), 58.2 (s, O-$\mathbf{C}H_2$), 70.8 (s, O-$\mathbf{C}H_3$). $^{27}Al\{^1H\}$ NMR: δ = 124.0 ppm (br,s, $W_{1/2}$ = 1840 Hz); solution in d_8-toluene.

3 (1.0 g, 45.7% yield), mp 100 °C. X-ray quality crystals were obtainable. Anal. Calc. (Found) for $C_6H_{18}A1C1_2P$: C, 32.90 (32.60); H, 8.28 (8.30); C1,32.37 (32.20); P, 14.14 (14.00). ^1H NMR: $\delta = -$ 0.86 ppm (br, s, Al(C$\mathbf{H}_3)_2$, 6 H), 1.90 ppm (d, (C$\mathbf{H}_3)_4P^+$, 12 H, $^2J_{PH}$ = 14.10 Hz). $^{13}C\{^1H\}$ NMR: $\delta = -$ 10.6 ppm (br,s, Al$\mathbf{C}H_3$), 9.30 ppm (d, ($\mathbf{C}H_3)_4P^+$, $^2J_{PC}$ = 56.0 Hz). $^{27}Al\{^1H\}$ NMR: δ = 152.0 ppm (br,s, $W_{1/2}$ = 2450 Hz). $^{31}P\{^1H\}$ NMR: δ = 24.0 ppm (s); solution in d_3-CD_3CN.

Results and discussion

Following the same synthetic protocols as already reported for donor–acceptor adducts of $[R_nCl_{3-n}Al{\bullet}P(Si(CH_3)_3)_3]$ ($n = 0,1,2,3$).[12,13] The reaction of tris(trimethylsilyl)phosphine, $P(Si(CH_3)_3)_3$, with dimethylaluminum chloride, $(CH_3)_2AlCl$, in *n*-hexane afforded the complex $([(CH_3)_3Si)_3P{\bullet}Al(CH_3)_2Cl])$ (**1**) (Figure 1), as a white precipitate ([$^{31}P\{^1H\}$ = −246.77 ppm]; [$^{27}Al\{^1H\}$ = 160.0]).

As expected, an inspection of the $^{31}P\{^1H\}$ and $^{27}Al\{^1H\}$ spectra of adduct, $([(CH_3)_3Si)_3P{\bullet}Al(CH_3)_2Cl])$ is in agreement with data reported for the adducts, $[R_nCl_{3-n}Al{\bullet}P(Si(CH_3)_3)_3]$ ($n = 0,1,2,3$).[12,13] It is surprising, stirring the solution of the adduct $([(CH_3)_3Si)_3P{\bullet}Al(CH_3)_2Cl])$ in 1,2-dimethoxyethane (monoglyme) for 12 h revealed two different types of

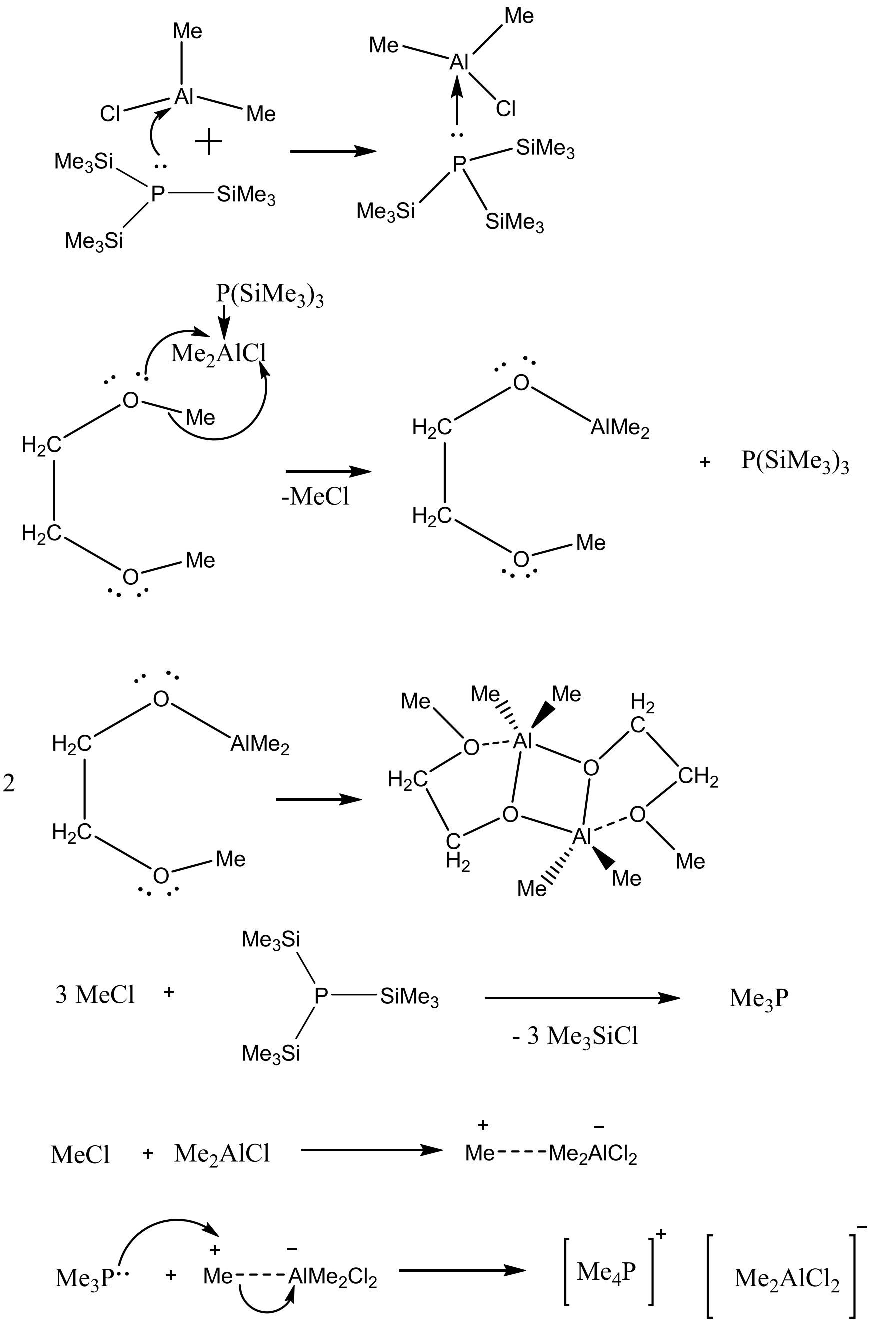

Figure 1. A postulated mechanism to explain the formation of tetramethyl phosphonium dichlorodimethylaluminate.

structures, the first crystal structure is reported previously and known as bis(2,2-methoxy-ethanolato-O,O′)-tetramethyl-dialuminum, $[(CH_3)_2AlO(CH_2)_2OCH_3]_2$ (**2**),[30,32] the second crystal structure is a novel tetramethylphosphonium dichlorodimethylaluminate, $[(CH_3)_4P]^+[(CH_3)_2AlCl_2]^-$ (**3**) ($[^{31}P\{^1H\} = 24.0\,ppm]$) (Figure 1), the cleavage of 1,2-dimethoxyethane are analogous to the reaction reported in previous literature,[28] wherein carbon–oxygen bond fission results from stirring the solution of the adduct ($[(CH_3)_3Si)3P{\bullet}Al(CH_3)_2Cl]$) in 1,2-dimethoxyethane, the oxophilic character of $(CH_3)_2AlCl$ enables coordination with 1,2-dimethoxyethane by the Lewis acidic center (Al^{3+}) through the formation of donor–acceptor complexes. The complexes undergo cleavage to form (Al-O) complexes via methyl chloride elimination,[28] the reaction of tris(trimethylsilyl)phosphine with methyl chloride via cleavage of the weak polar Si-P bonds,[8] leads to form trimethylphosphine and then continue to form a novel tetramethylphosphonium dichlorodimethylaluminate (**3**). Further a mechanistic and thermodynamics studies, quantum chemical calculations, and the biological activity of the discussed material are still in progress under consideration in my laboratory. The phosphorus NMR of **3** is in agreement with the NMR data reported for other phosphonium salts, $[(CH_3)_4P]X$.[43–48] The $^{27}Al\{^1H\}$ NMR spectrum of compound **2** exhibits a broad peak at 124.0 ppm. As can be taken from the literature,[30,32] this region is attributed to a five coordinated aluminum. On the other hand, the $^{27}Al\{^1H\}$ NMR peak of compound **3** at 152.0 ppm is assigned to a four coordinated aluminum.[30] The $^{27}Al\{^1H\}$ NMR parameters of similar aluminum compounds together with their respective coordination number were reported in previous publications,[30,32,49,50] in that the chemical shifts values δ (^{27}Al) have been taken as an indicator for the coordination number of aluminum atoms. Chemical shifts for both the $^{13}C\{^1H\}$- and ^1H NMR spectra of the compound **2** which were already reported previously are similar.[51,52] The ^1H NMR of compound **3** exhibits two major peaks at -0.86 ppm (br,s, $Al(\mathbf{CH_3})_2$, 6 H) and 1.90 ppm (d, $(\mathbf{CH_3})_4P^+$, 12 H, $^2J_{PH} = 14.10$ Hz) are attributed for $\mathbf{H_3}C$–Al and $\mathbf{H_3}C$–P, respectively. $^{13}C\{^1H\}$ NMR of compound **3** shows also two major peaks at -10.6 ppm (br,s, Al-CH_3) and 9.30 ppm (d, $(\mathbf{C}H_3)_4P^+$, $^2J_{PC} = 56.0$ Hz). Based on the assignment given in the literature for compound types $(CH_3)_4PX$[43–48] and compound $[Te(CH_3)_3]^+[Al(CH_3)_2Cl_2]^-$,[53] the $^{13}C\{^1H\}$- and ^1H NMR spectra of complex $[(CH_3)_4P]^+[(CH_3)_2AlCl_2]^-$ (**3**) can be interpreted similarly.

After the resolution and refinement of the molecular structure (**2**), the structural study shows that dimer aluminum oxo compound (**2**) (Figure 2, Table 1) crystallizes in the monoclinic space group $P2_1/n$. The unit cell with lattice constants a = 7.404, b = 14.205, c = 7.772 Å, and $\beta = 101.62°$ includes two formula units.

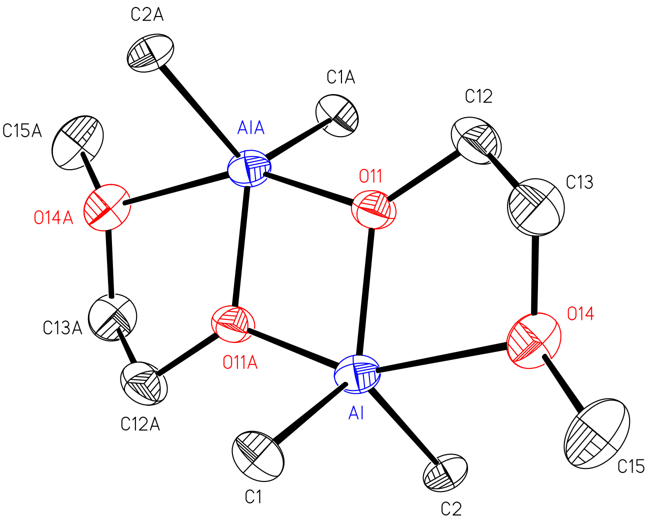

Figure 2. Molecular structure of **2**. Thermal ellipsoids are at 30% probability, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al … Al 2.941(15), Al-C1 2.017(2), Al-C2 2.004(2), Al-O11 1.832(18), AlA-O11 1.905(18), Al-O14 2.208(2), O14-C15 1.434(3), O14-C13 1.422(4), O11-C12 1.423(3), C12-C13 1.483(4), O11-Al-C1 118.42(10), O11-Al-C2 120.47(9), O14-Al-C1 94.26(9), O14-Al-C2 90.57(9), C1-Al-C2 120.40(11).

Table 1. Crystallographic data and structure refinement for compounds **2** and **3**.

Compound	2	3
Formula	$C_{10}H_{26}Al_2O_4$	$C_6H_{18}AlCl_2P$
Mr (g.mol^{-1})	264.27	219.05
Melting point (K)	393	373
Crystal size (mm)	0.50 × 0.40 × 0.20	0.50 × 0.50 × 0.30
T (K)	173(2)	173(2)
λ(Å)	0.71073	0.71073
Diffractometer	$P2_1$	$P2_1$
Colour and crystal shape	Colorless plates	Colorless block
Crystal system	Monoclinic	Monoclinic
Space group	(*P21/n* (No. 14)	(*P21/c* (No. 14)
Unit cell dimensions *a* (Å)	7.4039 (19)	7.522 (3)
b (Å)	14.205 (3)	11.644 (2)
c (Å)	7.772 (2)	14.841 (4)
α (°)	90	90
β (°)	101.62 (2)	99.32 (3)
γ (°)	90	90
Volume (Å^3)	800.7 (3)	1282.7 (7)
Z	2	4
D_{calc} (Mg/m^3)	1.096	1.134
μ (mm^{-1})	0.180	0.647
F(000)	288	464
θ-Range(°) for data collection	2.87–26.00	2.23–25.00
Limiting indices		
	$0 \le h \le 9$ $-17 \le k \le 17$ $-9 \le l \le 9$	$0 \le h \le 8$ $0 \le k \le 13$ $-17 \le l \le 17$
Reflections collected	3309	2441
Independent reflections (R_{int})	1573 (0.0433)	2258 (0.0457)
Data/restraints/parameters	1573/0/76	2258/0/97
Goodness-of-fit (GOF)	1.074	1.092
Final *R1/wR2* with $[I > 2\sigma(I)]$	0.0584, 0.1824	0.0318, 0.0922
Final *R1/wR2* indices (all data)	0.0652, 0.1876	0.0365, 0.0946
Largest diff. peak and hole (eÅ^{-3})	0.562 and −0.312	0.317 and −0.265

It is obvious by inspection of the previous works that the molecular structure (**2**) is studied and is available in the literature.[30,32] The aluminum alkoxide which here can best be described quite conventionally as a distorted trigonal bipyramid. The molecule consists of two fused five-membered rings and contains a central Al_2O_2 four-membered ring. The molecular structure data for (**2**) as already published previously byBestmann and Schobert[30] shows two methyl groups and an oxygen atom (O11) are located in the equatorial plane. The oxygen atom O11 is sited over a center of inversion and occupies an apical site of the second AlA atom with a longer AlA-O11 distance (+0.073 Å). Since the bond distance A1-O14 is 0.376 Å longer than the AI-O11 distance, O14 is even more weakly bonded to aluminum.[30] The length of weak dative bonds in organo aluminum alkoxide shows a temperature dependence in the solid-state that is distinctively different from the common effect of liberation and is interpreted as being caused by thermal excitation.[32] The packing of the molecular structure (**2**) in the unit cell is illustrated in Figure 3. There are no intermolecular contacts less than the van der Waals distances. One should mention that in the four-membered ring of **2** the intramolecular distance Al···Al is 2.94(15) Å. Concerning this value, both atoms approach each other to such an extent that the element–element distance of metallic aluminum (2.863 Å) is almost achieved.[23,54,55]

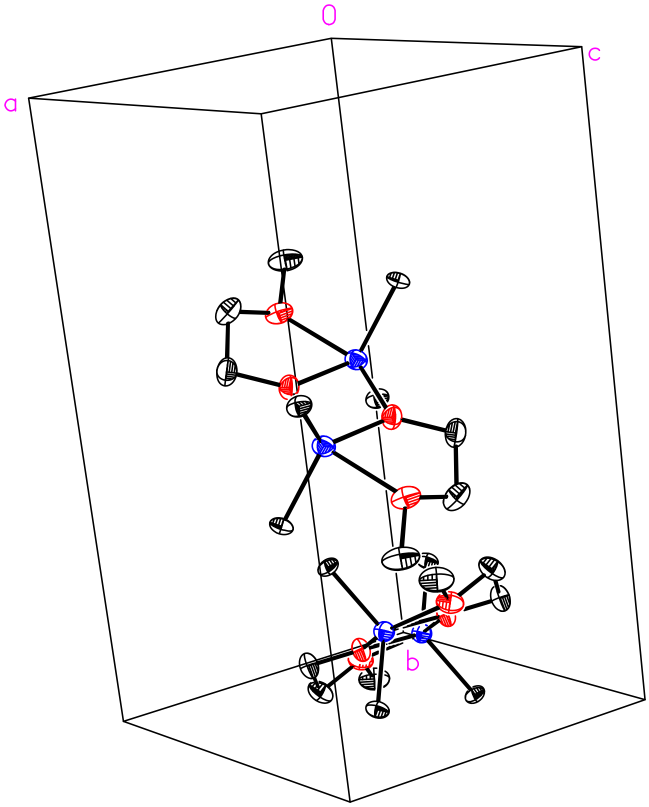

Figure 3. Unit cell contents of molecular structure **2**. Thermal ellipsoids are at 30% probability, hydrogen atoms are omitted for clarity.

The resolution and refinement of the molecular structure (**3**) (Figure 4, Table 1) crystallize in the monoclinic space group $P2_1/c$. The unit cell with lattice constants a = 7.522, b = 11.644, c = 14.841 Å, and $\beta = 99.32°$ includes four formula units. The mean values of the bond lengths are P-C 1.787 Å, Al-Cl 2.224 Å, and Al-C 1.966 Å. The results showed the presence of phosphonium aluminate salt $[(CH_3)_4P]^+$ $[(CH_3)_2AlCl_2]^-$ in the solid-state; the compound is built up of tetramethylphosphonium cations and dichlorodimethylaluminate anions (**3**) (Figure 4). Tetramethylphosphonium dichlorodimethylaluminate (**3**) is isostructural with tetramethylarsonium dichlorodimethylgallate (**A**).[56] Trimethylgallium reacts with five-coordinate arsenic (dichlorotrimethyl-λ^5–arsane) directly to produce tetramethylarsonium dichlorodimethylgallate (**A**).[56] A new member of these salt family was obtained with aluminum in place of gallium and phosphorus in place of arsenic by different synthesis methods (Figure 1). The effect of P/As and Al/Ga total substitution is remarkable in the tetrahedra (Table 2). Both phosphorus and aluminum are tetrahedrally surrounded in organophosphonium-based cations and organoaluminium-based anions. The geometry of the dichlorodimethylaluminate anion shows a distorted tetrahedron (Figure 4, Table 2).

The results obtained in this study are the first report of phosphonium salt-containing organophosphonium-based

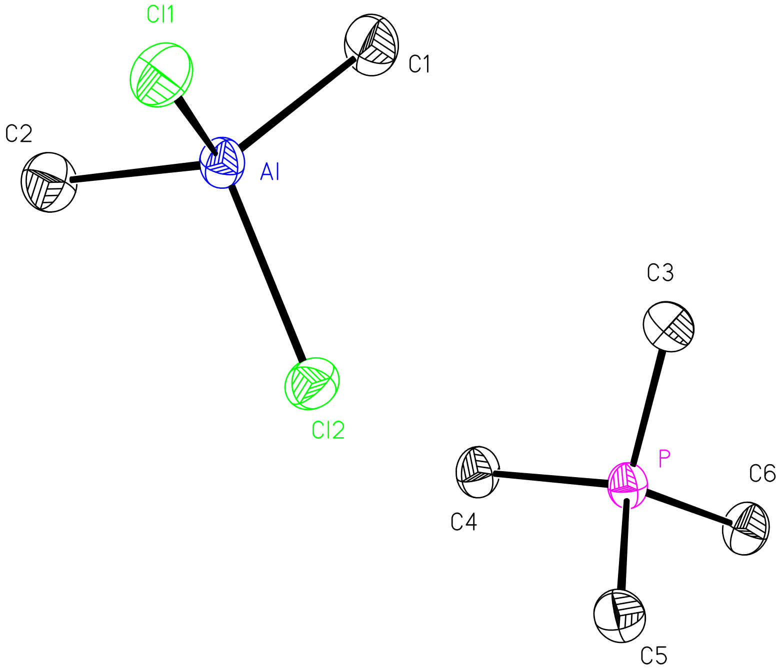

Figure 4. Molecular structure of **3**. Thermal ellipsoids are at 30% probability, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al … P 5.474(2). Tetramethylphosphonium: P-C3 1.785(2), P-C4 1.792(2), P-C5 1.780(2), P-C6 1.789(2), C3-P-C4 109.09(11), C5-P-C6 109.14(10), C6-P-C4 109.35(11), C3-P-C6 109.80(10), C5-P-C3 109.48(10), C5-P-C4 109.97(10). Dichlorodimethylaluminate: Al-C1 1.961(2), Al-C2 1.970(2), Al-Cl1 2.224(1), Al-Cl2 2.223(1), C1-Al-Cl1 107.94(9), C1-Al-Cl2 108.95(8), C2-Al-Cl1 108.51(8), C2-Al-Cl2 108.85(8), Cl2-Al-Cl1 101.94(4), C1-Al-C2 119.25(10).

Table 2. Comparison of characteristic crystallographic data, average bond lengths(Å), and bond angles (°) for compounds **A** and **3**.

Compound	A	3
Formula	$C_6H_{18}GaCl_2As$	$C_6H_{18}AlCl_2P$
Mr (g.mol^{-1})	305.8	219.05
Crystal system	Monoclinic	Monoclinic
Space group	(*P21/c* (No. 14)	(*P21/c* (No. 14)
Unit cell dimensions *a* (Å)	7.511 (2)	7.522 (3)
b (Å)	11.734 (3)	11.644 (2)
c (Å)	14.908 (4)	14.841 (4)
α (°)	90	90
β (°)	99.75 (3)	99.32 (3)
γ (°)	90	90
Volume (Å^3)	1294.9 (6)	1282.7 (7)
Z	4	4
D_{calc} (Mg/m^3)	1.568	1.134
As/P-C (Å)	1.923	1.787
Ga/Al-C (Å)	1.980	1.966
Ga/Al-Cl (Å)	2.277	2.224
C-As/P-C (°)	109.47	109.47
C-Ga/Al-C (°)	125.35	119.25
Cl-Ga/Al-Cl (°)	99.68	101.94
C-Ga/Al-Cl (°)	107.22	108.56

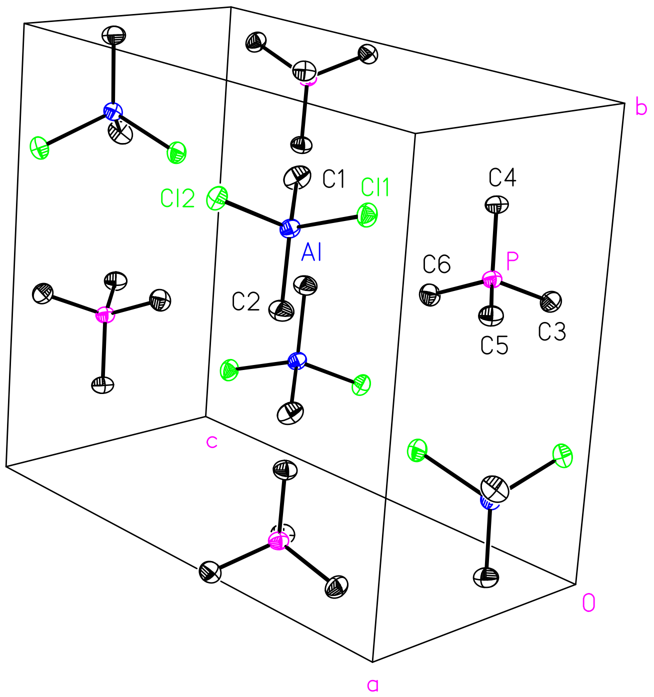

Figure 5. Unit cell contents of molecular structure **3**. Thermal ellipsoids are at 30% probability, hydrogen atoms are omitted for clarity.

cations and organoaluminium-based anions. Geometric parameters in the organophosphonium-based cation, $[(CH_3)4P]^+$ (Figure 4, Table 1) are in the usual ranges, with a mean P-C bond distance of 1.787 Å. It tallies the mean value of 1.790 Å as determined by X-ray structure analyses for the P-C bond in tetramethylphosphonium cations.[45,47] Furthermore, an organoaluminium-based anion $Al(CH_3)_2Cl_2]^-$ (Figure 4), are also in the usual ranges, with both mean Al-Cl and Al-C bond distances of 2.223 and 1.966 Å, respectively. Whereas similar mean values were found in $[Te(CH_3)_3]^+[Al(CH_3)_2Cl_2]^-$ (2.221 and 1.982 Å).[53] The packing of the molecular structure (**3**) in the unit cell is illustrated in Figure 5. There are no intermolecular contacts less than van der Waals distances. At 5.474 Å, the shortest interionic distance between the phosphorus atom and aluminum atom, however, is about twice as long as the corrected sum (2.36 Å) of the corresponding covalent radii of aluminum and phosphorus, estimated using the empirical formula of Modified Schomaker–Stevenson rule by Blom and Haaland.[23,57]

Conclusion

The experimental procedure and results presented in this article are very important for researchers who work on phosphonium salt. For the first time, herein the synthesis and X-ray crystal structure of $[(CH_3)_4P]^+[(CH_3)_2AlCl_2]^-$ has been reported. The title compound is unique in that phosphonium salts contain organophosphonium-based cations and organoaluminium-based anions that offer interesting synthetic possibilities in the main group chemistry. This method brings forward a broad idea for the synthesis of other tetramethylphosphonium dialkyldihaloaluminate compounds.

Supplementary Information (SI)

The structures solved from the crystallographic data of the compounds **2** and **3** were deposited to the Cambridge Crystallographic Data Centre (CCDC) under numbers 1908162 and 1908163, respectively. Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Ethical statement

All ethical guidelines have adhered.

Conflict of interest

The author declares that he has no conflict of interest.

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References

1. Wittig, G.; Weigmann, H.-D.; Schlosser, M. Abwandlung Der Phosphylen-Methodik; Zugleich III. Mitteil. über Phosphin-Alkylene Als Olefinbildende Reagenzien. *Chem. Ber.* **1961**, *94*, 676–689.
2. Wittig, G.; Schoellkopf, U. Methylenecyclohexane. *Org. Synth* **1960**, *40*, 66–67.
3. Wittig, G.; Schöllkopf, U. Über Triphenyl-Phosphin-Methylene Als Olefinbildende Reagenzien (I. Mitteil.). *Chem. Ber.* **1954**, *87*, 1318–1330. DOI: 10.1002/cber.19540870919.

4. Wittig, G.; Haag, W. Über Triphenyl-Phosphinmethylene Als Olefinbildende Reagenzien (II. Mitteil.). *Chem. Ber.* **1955**, *88*, 1654–1666. DOI: 10.1002/cber.19550881110.
5. Klein, H. F. From Tetramethylphosphonium Bromide. *Inorg. Synth* **1978**, *18*, 138–140.
6. Cassar, L.; Foà, M. Nickel-Catalyzed Synthesis of Phosphonium Salts. *J. Organomet. Chem* **1974**, *74*, 75–78. DOI: 10.1016/S0022-328X(00)83762-6.
7. Werner, T. Phosphonium Salt Organocatalysis. *Adv. Synth. Catal.* **2009**, *351*, 1469– 1481. DOI: 10.1002/adsc.200900211.
8. Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. Tris(Trimethylsilyl)Phosphine and Lithium Bis(Trimethylsilyl)Phosphine Bis(Tetrahydrofuran). *Inorg. Synth* **1990**, *27*, 243–249.
9. Becker, G.; Ditten, G.; Hubler, K.; Hubler, U.; Merz, K.; Niemeyer, M.; Seidler, N.; Westerhausen, M.; Zheng, Z. The Function of the Trimethylsilyl Substituent in the Syntheses of Low-Valent Phosphorus and Arsenic-Containing Compounds. *Organosilicon Chemistry* **1996**, *11*, 161–186.
10. Becker, G.; Brombach, H.; Horner, S. T.; Niecke, E.; Schwarz, W.; Streubel, R.; Würthwein, E.-U. Synthesis and Structure of K$^+$ [^{i}PrN = C=P]$^-$, a 1-Aza-3lambda3-Phospha-3-Allenide. *Inorg. Chem.* **2005**, *44*, 3080–3086. DOI: 10.1021/ic048162+.
11. Becker, G.; Ditten, G.; Horner, S.; Maulitz, A. H.; Wiirthwein, E.-U. Differing Affinities of the Triorganylsilyl and -Stannyl Substituents for Oxygen or Nitrogen, and Phosphorus, Respectively. *Ovganosilicon Chemistry* **2003**, *5*, 307–311.
12. Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. A. Aluminum-Phosphorus Chemistry: preparation and Structural Characterization of [Et-Al•P(SiMe$_3$)$_2$]$_2$, Et(C1)$_2$Al•P(SiMe$_3$)$_3$, and i-Bu$_2$(Cl)Al•P(SiMe$_3$)$_3$. *Organometallics* **1993**, *12*, 3333–3339. DOI: 10.1002/chin.199349234.
13. Kuczkowski, A.; Schulz, S.; Nieger, M.; Schreiner, P. R. Experimental and Computational Studies of R$_3$Al-ER$'_3$ (E = P, as, Sb, Bi; R = Et, t-Bu; R$'$ = SiMe$_3$, ^{i}-Pr) Donor-Acceptor Complexes: role of the Central Pnictine and the Substituents on the Structure and Stability of Alane Adducts. *Organometallics* **2002**, *21*, 1408–1419. DOI: 10.1021/om0200205.
14. Blackman, C. S.; Carmalt, C. J.; O'Neill, S. A.; Parkin, I. P.; Apostolico, L.; Molloy, K. C. Dual-Source Chemical Vapour Deposition of Titanium(III) Phosphide from Titanium Tetrachloride and Tristrimethylsilylphosphine. *Appl. Surf. Sci* **2003**, *211*, 2–5. DOI: 10.1016/S0169-4332(03)00263-0.
15. Tawarah, K. M.; Jibril, I.; Bani-Fwaz, M. Z. Kinetics and Mechanism of the Photolytic CO-Substitutions of Cyclopentadienyl-(Dicarbonyl)Iron Thiocarboxylate Complexes, Cp ± Fe(CO)$_2$SCOR (Cp$'$ = C$_5$H$_5$, Bu*t*C$_5$H$_4$, 1,3-Bu$_2$*t*C$_5$H$_3$; R = Alkyl, Aryl). *Transition Met. Chem* **2000**, *25*, 659–663.
16. Nagahora, N.; Tokumaru, H.; Ikaga, S.; Hanada, T.; Shioji, K.; Okuma, K. Synthetic Studies on a Series of Functionalized Pyrylium Salts, 4-Chloro- and 4-Bromophosphinines. *Tetrahedron* **2018**, *74*, 1880–1887. DOI: 10.1016/j.tet.2018.02.053.
17. Karanam, P.; Reddy, G. M.; Koppolu, S. R.; Lin, W. Recent Topics of Phosphine-Mediated Reactions. *Tetrahedron Lett* **2018**, *59*, 59–76. DOI: 10.1016/j.tetlet.2017.11.051.
18. Floch, P. Phosphaalkene, Phospholyl and Phosphinine Ligands: New Tools in Coordination Chemistry and Catalysis. *Coord. Chem. Rev* **2006**, *250*, 627–681. DOI: 10.1016/j.ccr.2005.04.032.
19. Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. 2,2-Dimethylpropylidyne)Phosphine. *Inorg. Synth* **1990**, *27*, 249–253.
20. Lynam, J. M. Recent Advances in the Chemistry of Phosphaalkynes: Building Blocks for Novel Organophosphorus Compounds. *Organomet. Chem* **2007**, *33*, 170–178.
21. Chirila, A.; Wolf, R.; Slootweg, J. C.; Lammertsma, K. Main Group and Transition Metal-Mediated Phosphaalkyne Oligomerizations. *Coord. Chem. Rev* **2014**, *270-271*, 57–74. DOI: 10.1016/j.ccr.2013.10.005.
22. Bani-Fwaz, M. Z.; Fazary, A. E.; Becker, G. Synthesis, Crystal Structures, and Quantum Chemical Calculations of Novel Phosphonium Salt-1,5-Diphospha-3-Phosphonia-Tricyclo Pentane Cations. *J. Organomet. Chem* **2017**, *846*, 51–65. DOI: 10.1016/j.jorganchem.2017.05.052.
23. Bani-Fwaz, M. Z.; Fazary, A. E.; Becker, G. Synthesis and Crystal Structures of Dialkyl[1,1-Bis(Alkylchloroalanyl)Organylmethyl] Phosphine•Dialkylchloroalane(1/1) Complexes. *J. Coord. Chem* **2017**, *70*, 2224–2248. DOI: 10.1080/00958972.2017.1346248.
24. Bani-Fwaz, M. Z.; Fazary, A. E.; Becker, G. Synthesis, Crystal Structures, and Quantum Chemical Calculations of Trialkyl-Substituted 1λ^3,3λ^3,5λ^3-Triphospha Dewarbenzenes. *J. Mol. Struct* **2017**, *1146*, 380–401. DOI: 10.1016/j.molstruc.2017.05.144.
25. Bani-Fwaz, M. Z.; Fazary, A. E. Commentary on the Synthesis and Structures of Unsupported Cycloarsoxane Compounds. *Comments. Inorg. Chem* **2018**, *38*, 36–58. DOI: 10.1080/02603594.2018.1423618.
26. Bani-Fwaz, M. Z.; Fazary, A. E.; Becker, G. Crystal Structures and Quantum Chemical Calculations of Dichloro[4-(Dimethylamino)Phenyl]Arsine and Tris[4-(Dimethylamino)Phenyl]Arsine. *J. Mol. Struct* **2017**, *1149*, 560–568. DOI: 10.1016/j.molstruc.2017.08.020.
27. Zhao, L.; Hermann, M.; Holzmann, N.; Frenking, G. Dative Bonding in Main Group Compounds. *Coord. Chem. Rev* **2017**, *344*, 163–204. DOI: 10.1016/j.ccr.2017.03.026.
28. Lehmkuhl, H.; Schäfer, R. Metallorganische Verbindungen, XLV, Komplex-Bildung Und Reaktionen Von Methylaluminium-Verbindungen Unit Diglyme. *Justus* Liebigs Ann. *Chem.* **1967**, *705*, 23–31. DOI: 10.1002/jlac.19677050103.
29. Nöth, H.; Rurländer, R.; Wolfgardt, P. An Investigation of AlCl$_3$ Solutions in Ethers by ^{27}Al NMR Spectroscopy. *Z. Naturforsch. B* **1982**, *87b*, 29–37. DOI: 10.1515/znb-1982-0106.
30. Benn, R.; Rufińska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. ^{27}A1-NMR Spectroscopy: A Probe for Three-, Four-, Five-, and Sixfold Coordinated A1 Atoms in Organoaluminum Compounds. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 779–780. DOI: 10.1002/anie.198307791.
31. Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. ^{27}Al-NMR-Spektroskopie Zur Charakterisierung Von Organoaluminium-Verbindungen. *J. Organomet. Chem* **1987**, *333*, 155–168. DOI: 10.1016/0022-328X(87)85147-1.
32. Schumann, H.; Girgsdies, F.; Dechert, S.; Gottfriedsen, J.; Hummert, M.; Schutte, S.; Pickardt, J. Thermally Induced Lengthening of Weak Dative Bonds in Donor Functionalized Organoaluminum Alkoxides Observed by X-Ray Single Crystal Diffraction. *Z* Anorg. Allg. *Chem.* **2002**, *628*, 2625–2630. DOI: 10.1002/1521-3749(200212)628:12<2625::AID-ZAAC2625>3.0.CO;2-E.
33. Zhang, L.; Tang, Q.; Weiss, R. A.; Cavicchi, K. A. Synthesis and Characterization of Quaternary Phosphonium-Containing, Trithiocarbonate RAFT Agents. *Polym. Chem* **2014**, *5*, 5492–5500. DOI: 10.1039/C4PY00615A.
34. Bujdáková, H.; Bujdáková, V.; Májeková-Koščová, H.; Gaálová, B.; Bizovská, V.; Boháč, P.; Bujdák, J. Antimicrobial Activity of Organoclays Based on Quaternary Alkylammonium and Alkylphosphonium Surfactants and Montmorillonite. *Appl. Clay. Sci* **2018**, *158*, 21–28. DOI: 10.1016/j.clay.2018.03.010.
35. Chen, Y.; Tan, W.; Li, Q.; Dong, F.; Gu, G.; Guo, Z. Synthesis of Inulin Derivatives with Quaternary Phosphonium Salts and Their Antifungal Activity. *Int. J. Biol. Macromol* **2018**, *113*, 1273–1278. DOI: 10.1016/j.ijbiomac.2018.03.055.
36. Brunel, F.; Lautard, C.; di Giorgio, C.; Garzino, F.; Raimundo, J.-M.; Bolla, J.-M.; Camplo, M. Antibacterial Activities of Mono-, di- and Tri-Substituted Triphenylamine-Based Phosphonium Ionic Liquids. *Bioorg. Med. Chem. Lett* **2018**, *28*, 926–929. DOI: 10.1016/j.bmcl.2018.01.057.
37. Talbot, R. E.; Downward, B. L.; Haack, T. Tetrakishydroxymethyphosphonium Sulfate (THPS) a New, Environmentally Benign Biocide for Cooling Water Systems. *In International Water Conference Proceedings, Engineers' Society of Western Pennsylvania, Pittsburgh* **1998**, *59*, 561–568.

38. Aldridge, S.; Warwick, P.; Evans, N.; Vines, S. Degradation of Tetraphenylphosphonium Bromide at High pH and Its Effect on Radionuclide Solubility. *Chemosphere* **2007**, *66*, 672–676.
39. Schütze, M. Feinreinigung Von Gasen Mit Einem Hochaktiven Kupferkatalysator. *Angew. Cheme* **1958**, *70*, 697–699. DOI: 10.1002/ange.19580702206.
40. Kottke, T.; Stalke, D. Crystal Handling at Low Temperatures. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. DOI: 10.1107/S0021889893002018.
41. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr C Struct Chem* **2015**, *71*, 3–8. DOI: 10.1107/S2053229614024218.
42. Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal Structure Determination. *Acta Crystallogr. A Found. Adv.* **2015**, *A71*, 3–8. DOI: 10.1107/S2053273314026370.
43. Karsch, H. H. Funktionelle Trimethylphosphanderivate, XV, (Chlormethyl)-Dimethylphosphan. *Chem. Ber.* **1982**, *115*, 823–827. DOI: 10.1002/cber.19821150248.
44. Karsch, H. H. FUNKTIONELLE TRIMETHYLPHOSPHINDERIVATE 16. Über Die Reaktion Von Tertiären Phosphinen Mit Methylendihalogeniden. *Sulfur Silicon Relat. Elem* **1982**, *12*, 217–225. DOI: 10.1080/03086648208077450.
45. Haije, W. G.; Dobbelaar, J. A. L.; Maaskant, W. J. A. The Structure of Tetramethylphosphonium Dicopper Pentachloride. *Acta Crystallogr. C Cryst. Struct. Commun.* **1986**, *C42*, 1485–1487. DOI: 10.1107/S0108270186091758.
46. Evans, D. J.; Leigh, G. J.; Macdonald, C. J. Carbon-13 and Related NMR Chemical Shifts in Alkylammonium and Alkylphosphonium Salts. *Magn. Reson. Chem.* **1990**, *28*, 711–714. DOI: 10.1002/mrc.1260280810.
47. Margraf, G.; Lerner, H.-W.; Bolte, M. Tetramethylphosphonium Chloride Hydrate. *Acta* Crystallogr. *E* Struct. *Rep. Online* **2002**, *E58*, o546–o547. DOI: 10.1107/S1600536802006785.
48. Wojtas, M.; Jakubas, R. Structure and Properties of $[(CH_3)_4P]_3[Sb_2Cl_9]$ and $[(CH_3)_4P]_3[Bi_2Cl_9$. *J. Phys: Condens. Matter* **2004**, *16*, 7521–7534.]. DOI: 10.1088/0953-8984/16/41/029.
49. Samadi-Maybodi, A.; Nejad-Darzi, S. K. H.; Bijanzadeh, H. ^{31}P and ^{27}Al NMR Studies of Aqueous (2-Hydroxyethyl) Trimethylammonium Solutions Containing Aluminum and Phosphorus. *Spectrochim. Acta. A* **2009**, *72*, 382–389. DOI: 10.1016/j.saa.2008.10.002.
50. Goudarzi, N.; Goodarzi, M.; Chamgangali, M. A.; Bagherian, G. Study of the Ethanolic Tributylmethylammonium Aluminosilicate Solutions Using ^{27}Al NMR. *J. Mol. Struct* **2009**, *930*, 2–8. DOI: 10.1016/j.molstruc.2009.04.017.
51. Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. Koordinations-Komplexe Lewis-Basischer Dialkylaluminiumalkoxide Mit Trialkylaluminium. *J. Organomet. Chem* **1987**, *333*, 169–180. DOI: 10.1016/0022-328X(87)85148-3.
52. Schumann, H.; Frick, M.; Heymer, B.; Girgsdies, F. Intramolecularly Stabilized Organoaluminium and Organogallium Compounds: synthesis and X-Ray Crystal Structures of Some Dimethylaluminium and -Gallium Alkoxides Me_2M-O-R-OR' and Amides Me_2M-NH-R-OR. *J. Organomet. Chem* **1996**, *512*, 117–126. DOI: 10.1016/0022-328X(95)05917-E.
53. Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. Alkylation of Tellurium Tetrachloride by Trimethylaluminum. Synthesis and Molecular Structure of $[Te(CH_3)_3][Al(CH_3)_2Cl_2]$: a Novel Organotellurium-Aluminum Oligomer. *J. Crystallogr. Spectrosc. Res* **1989**, *19*, 433–438. DOI: 10.1007/BF01185380.
54. Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G. Consistent Van Der Waals Radii for the Whole Main Group. *J Phys Chem A* **2009**, *113*, 5806–5812. DOI: 10.1021/jp8111556.
55. Uhl, W. Tetrakis[Bis(Trimethylsilyl)Methyl]Dialan(4), Eine Verbindung Mit Aluminium—Aluminium-Bindung. *Z. Naturforsch. b* **1988**, *43b*, 1113–1118. DOI: 10.1515/znb-1988-0905.
56. Hausen, H. D.; Guder, H. J.; Schwarz, W. Die Kristallstrukturen Von Tetramethylarsonium-Dichlorodimethylgallat $[(CH_3)_4As]^+[(CH_3)_2GaCl_2]^-$ Und Tetramethylarsonium-Trichloromonomethylgallat $[(CH_3)_4As]^+[CH_3GaCl_3]$. *J. Organomet. Chem* **1977**, *132*, 37–43. DOI: 10.1016/S0022-328X(00)92512-9.
57. Blom, R.; Haaland, A. A Modification of the Schomaker—Stevenson Rule for Prediction of Single Bond Distances. *J. Mol. Struct* **1985**, *128*, 21–27. DOI: 10.1016/0022-2860(85)85036-5.