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Research Article

Dichlorophosphoranides Stabilized by Formamidinium Substituents

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Dichlorophosphoranides featuring *N*,*N*-dimethyl-*N*′-arylformamidine substituents were isolated as individual compounds. Dichlorophosphoranide **9** was prepared by the multicomponent reaction of *C*-trimethylsilyl-*N*,*N*-dimethyl-*N*′-phenylformamidine and *N*,*N*-dimethyl-*N*′-phenylformamidine with phosphorus trichloride. Its molecular structure derived from a single-crystal X-ray diffraction was compared to the analogous dibromophosphoranide prepared previously by us by the reaction of phosphorus tribromide with *N*,*N*-dimethyl-*N*′-phenylformamidine. It was shown that a chlorophosphine featuring two *N*,*N*-dimethyl-*N*′-mesitylformamidine substituents reacted with hydrogen chloride to form dichlorophosphoranide **11**. Its molecular structure was also determined by X-ray analysis and compared with that of closely related dichlorophosphoranide **C**.

1. Introduction

Phosphoranides **A** are hypervalent anionic phosphorus(III) compounds formally possessing a 10-electron valence shell and a distorted pseudotrigonal bipyramidal arrangement at the phosphorus atom. The electronegative ligands at phosphines make nucleophilic addition possible to afford stable phosphoranides (Figure 1).

The first isolated phosphoranide has been prepared by the reaction of tetrapropylammonium bromide with phosphorus tribromide, and its structure has been unambiguously determined by a single-crystal X-ray diffraction study [1, 2]. Later, tetrachlorophosphoranides and tetrafluorophosphoranides were prepared, with tetrafluorophosphoranide being the most stable derivative [3]. *N*-heterocyclic carbenes are known to be suitable for stabilization of high-coordinated P atoms. The reaction of a sterically hindered *N*-heterocyclic carbene with PCl_3 in hexane affords a high yield of phosphoranide **B**. The imidazoliumyl substituent efficiently stabilizes phosphoranides. Another example is phosphoranide **C** in which the imidazolium moieties serve for stabilization [4, 5]. In our previous publication, we have described the synthesis of dibromophosphoranide **3** by the reaction of *N*,*N*-dimethyl-*N*′-phenylformamidine **1** with phosphorus tribromide in a 3 : 1 ratio. Its structure was established by X-ray diffraction analysis. Based on DFT calculations, the mechanism for formation of phosphoranide **3** has been suggested (Scheme 1) [6].

The final step of the proposed mechanism is the reaction of dibromophosphine **2** with *N*,*N*-dimethyl-*N*′-phenylformamidine. It should be noted that other P(III) halides, such as phosphorus trichloride, dichlorophosphines, and monochlorophosphines, do not react with the formamidines. Earlier, we were unable to check the mechanism, as dibromo(dichloro)phosphines featuring the formamidine substituent were unavailable. Recently, we have developed a method for the synthesis of *C*-trimethylsilyl-*N*,*N*-dialkyl-*N*′-arylformamidines and studied their reactions with phosphorus trichloride and chlorophosphines. A set of chlorophosphines featuring two formamidine substituents were isolated as stable compounds [7]. We assumed that dichlorophosphines featuring the formamidine substituents can be prepared by this method as well. It will allow

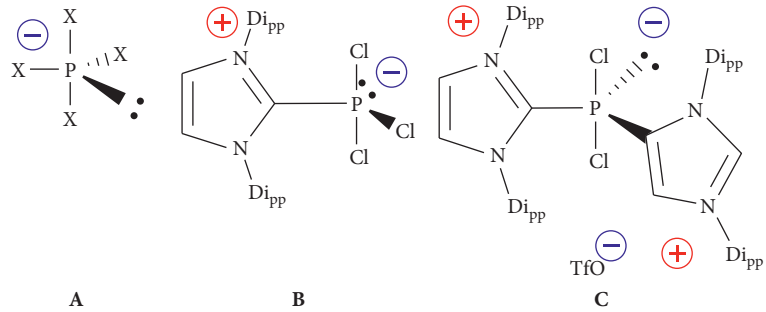
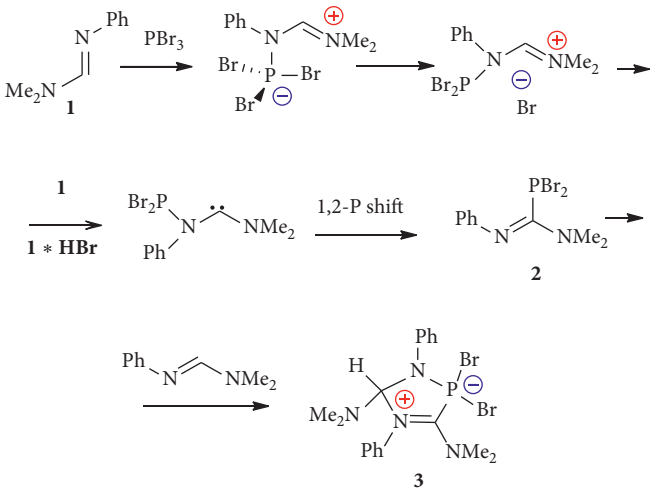


Figure 1: Examples of phosphoranides stabilized by *N*-heterocyclic carbene ligands.



Scheme 1: Mechanism proposed for formation of dibromophosphoranide **3**.

investigation of the proposed mechanism and development of a method for the synthesis of phosphoranides.

2. Materials and Methods

All procedures with air- and moisture-sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus and were uncorrected. ^{1}H spectra were recorded on a Bruker Avance DRX 500 (500.1 MHz) or Varian VXR-300 (299.9 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.8 MHz) spectrometer. ^{31}P NMR spectra were recorded on a Varian VXR-300 (121.4 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to internal TMS (for ^{1}H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Chromatography was performed on silica gel Gerudan SI_{60}. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine.

2.1. X-ray Structure Determination. Crystal data for **9**: ($C_{18}H_{23}Cl_2N_4P$), $M = 397.29$, triclinic, space group P-1, a = 9.3377(2), $b = 9.9530(2)$, $c = 12.3654(3)$ Å, $\alpha = 108.414(1)$, $\beta = 106.412(1)$, $\gamma = 101.860(1)^\circ$, $V = 989.57(4)$ Å^3, $Z = 2$, $d_c = 1.33$, μ 0.418 mm^{-1}, F(000) 416, crystal size ca. 0.33 × 0.47 × 0.54 mm. All crystallographic measurements were performed at 123K on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensity data were collected using Mo-K_α radiation ($\lambda = 0.71078$ Å). The intensities of 22667 reflections were collected (4183 unique reflections, $R_{merg} = 0.033$). Convergence for **9** was obtained at $R_1 = 0.0294$ and wR = 0.058 for 3520 observed reflections with $I \geq 3\sigma(I)$; GOF = 0.9332, $R_1 = 0.0360$, and wR = 0.0617 for all 4167 data, 226 parameters, and the largest and minimal peaks in the final difference map 0.34 and −0.22 e/Å^3.

Crystal data for **11**: ($C_{24}H_{35}Cl_2N_4P_1$), $M = 481.45$, orthorhombic, space group $Pna2_1$, a = 11.8655(3), $b = 14.1280(3)$, $c = 15.3685(3)$ Å, $V = 2576.31(10)$ Å^3, $Z = 4$, $d_c = 1.241$, μ 0.333 mm^{-1}, F(000) 1024, crystal size ca. 0.25 × 0.27 × 0.48 mm. All crystallographic measurements were performed at 123K on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensities of 30253 reflections were collected (4944 unique reflections, $R_{merg} = 0.039$). Convergence for **11** was obtained at $R_1 = 0.0287$ and wR = 0.0484, GOF = 0.9187 for 4259 observed reflections with $I \geq 3\sigma(I)$; GOF = 0.9187, $R_1 = 0.0363$, and wR = 0.0525 for all 4923 data, 285 parameters, the largest and minimal peaks in the final difference map 0.41 and −0.31 e/Å^3. The structures were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the SIR97 and Crystals program package [8, 9].

1,1-Bis(dimethylamino)-*N*,*N*-diisopropyl-*N*′-4-mesityl-phosphine-carboximidamide selenide (5a): To a frozen solution of **4a** (1.31 g, 5 mmol) in Et_2O (15 mL), a solution of PCl_3 (0.69 g, 5 mmol) in diethyl ether (15 mL) was added. The reaction mixture was allowed to warm to ambient temperature (15°C) with stirring. The solvent was evaporated. Benzene (5 mL) was added to the residue, and then, a solution of dimethylamine (900 mg, 20 mmol) in benzene (6 mL) was added. The mixture was stirred for 15 min, and selenium (500 mg, 6 mmol) was added. The resulting suspension was stirred for 1 h at 15°C. The insolubles were filtered off and washed with benzene (2 × 5 mL), and the filtrate was evaporated. The residue was purified by silica gel plate chromatography. Yield, 60%. R_f 0.2–0.45 (CH_2Cl_2–hexane 1 : 1), m.p. 116–117°C; ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$): $\delta = 65.7$ ($J_{PSe} = 793$ Hz) ppm; ^{1}H NMR

(300 MHz, $CDCl_3$): $\delta = 2.10$ (s, 6 H, CH_3), 2.23 (s, 3 H, CH_3), 2.84 (d, $J = 2.7$ Hz), 2.87 (s, 18 H, NCH_3), 6.77 (s, 2 H, CH) ppm; ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 18.6$ (s, CH_3), 20.2 (s, CH_3), 37.9 (s, CH_3), 39.8 (s, CH_3), 126.1 (s, $_{ipso}$-C), 127.6 (s, CH), 129.9 (s, $_{ipso}$-C), 145.3 (d, $J = 21$ Hz, $_{ipso}$-C), 150.5 (d, $J = 155$ Hz, CN); EI-MS 387–100% $[M+2]^+$; elemental analysis calcd (%) for $C_{16}H_{29}N_4PSe$ (387.37) C 49.61, H 7.55, N 14.46, P 8.00; found: C 49.84, H 7.37, N 14.62, P 8.26.

1,1-Bis(dimethylamino)-*N*,*N*-dimethyl-*N*′-(4-mesityl)-phosphinecarboximidamide selenide (**5b**): To a frozen solution of PCl_3 (0.27 g, 2 mmol) in benzene (2 mL), a solution of *C*-silylformamidine **4b** (0.61 g, 1.9 mmol) in benzene (4 mL) was added with stirring. In 1 h, the reaction mixture was concentrated under vacuum. Benzene (3 mL) was added to the residue, and then, a solution of dimethylamine (0.41 g, 9 mmol) in benzene (3 mL) was added. The mixture was stirred for 15 min, and then, selenium (1.9 mmol) was added in two portions over 10 min. The resulting suspension was stirred overnight. The insolubles were filtered off and washed with benzene (2 × 2 mL), and the filtrate was evaporated. The residue was extracted with hexane (2 × 5 mL), the solvent was removed under reduced pressure, and the residual solid was purified by silica gel plate chromatography. Yield, 49%. R_f 0.5–0.8 (CH_2Cl_2 –hexane 1 : 1); m.p. 157–158°C (pentane); ^{31}P NMR {^1H} (202 MHz, $CDCl_3$): δ 60.0 ppm ($J_{PSe} = 793$ Hz). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.38$ (d, $J = 6.3$ Hz, 12 H, CH_3), 2.13 (s, 6 H, CH_3), 2.20 (s, 3 H, CH_3), 2.50 (d, $J = 10$ Hz, 12 H, NCH_3), 4.36 (br s, 2 H, CH), 6.78 (s, 2 H, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 19.1$ (s, CH_3), 20.2 (s, CH_3), 21.2 (s, CH_3), 37.8 (s, CH), 48.7 (s, CH_3), 124.75 (s, $_{ipso}$-C), 127.8 ($_{ipso}$-C), 127.9 (s, CH), 143.8 (d, $J = 8.8$ Hz, $_{ipso}$-C), 145.8 (d, $J = 88$ Hz, N=C); EI-MS 445-98.2% $[M+2]^+$; elemental analysis calcd (%) for $C_{20}H_{37}N_4PSe$ (443.48): C 54.17, H 8.41, N 12.63, P 6.98; found: C 53.89, H 8.88, N 13.01, P 7.32.

General procedure for synthesis of compounds (**6a** and **b**): To a solution of phosphineselenide **7** (1.9 mmol) in benzene (4 mL), a solution of tris(morpholino)phosphine (2 mmol) in benzene (8 mL) was added. The reaction mixture was stirred for 30 min, and then, the solvent was removed under reduced pressure until dryness. The residue was dissolved in pentane (10 mL), and the obtained solution was cooled to −12°C. After several hours, the precipitated solid was filtered off, the filtrate evaporated under vacuum, and the residue distilled to produce compound **6**.

1,1-Bis(dimethylamino)-*N*,*N*-dimethyl-*N*′-mesityl-phosphine-carboximidamide (**6a**): Yield, 93%. B.p. 120–122°C/0.05 Torr; m.p. 26–28°C; ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 92.4$, 88.7 (10 : 1) ppm; ^1H NMR (300 MHz, C_6D_6): $\delta = 2.22$ (s, 6 H, CH_3), 2.27 (s, 3 H, CH_3), 2.57 (s, 6 H, NCH_3) and 2.64 (d, $J = 8.7$ Hz, 12 H, NCH_3), 6.86 (s, 2 H, CH) ppm; ^{13}C NMR (125.7 MHz, C_6D_6) $\delta = 18.8$ (s, CH_3), 20.2 (s, CH_3), 38.1 (d, $J = 10$ Hz, CH_3), 40.6 (d, $J = 15$ Hz, CH_3), 125.3 (s, $_{ipso}$-C), 127.7 (s, CH), 127.9 (s, $_{ipso}$-C), 147.3 (s, $_{ipso}$-C), 160.0 (d, $J = 15$ Hz, N=C); elemental analysis calcd (%) for $C_{16}H_{29}N_4P$ (308.4): C 62.31, H 9.48, N 18.17, P 10.04; found: C 62.02, H 9.71, N 18.42, P 9.86.

1,1-Bis(dimethylamino)-*N*,*N*-diisopropyl-*N*′-mesityl-phosphine-carboximidamide (**6b**): Yield, 98%. B.p. 130°C/0.05 Torr, m.p. 59–60°C (pentane, −28°C); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 90.1$ ppm; ^1H NMR (500 MHz, C_6D_6): $\delta = 1.34$ (br s, 12 H, CH_3), 2.26 (s, 6 H, CH_3), 2.27 (s, 3 H, CH_3), 2.34 (d, $J = 8.5$ Hz, 12 H, NCH_3), 3.93 (br s, 2 H, CH), 6.85 (s, 2 H, CH) ppm; ^{13}C NMR (125.7 MHz, C_6D_6): 19.1 (d, $J = 4$ Hz, CH_3), 20.2 (s, CH_3), 20.9 (s, CH_3), 40.9 (d, $J = 15$ Hz, CH3), 47.8 (d, $J = 13$ Hz, CH), 124.1 (s, $_{ipso}$-C), 126.0 (s, $_{ipso}$-C), 127.9 (s, CH), 145.9 (s, $_{ipso}$-C), 157.5 (d, $J = 40$ Hz, N=C); elemental analysis calcd (%) for $C_{20}H_{37}N_4P$ (364.52): C 65.90, H 10.23, N 15.37, P 8.50; found: C 66.32, H 9.97, N 15.67, P 8.31.

1,1-Dichloro-*N*,*N*-diisopropyl-*N*′-mesityl-phosphine-carboximidamide (**7b**): To a solution of **6b** (360 mg, 1 mmol) in benzene (4 mL), PCl_3 (305 mg, 2.2 mmol) was added. The reaction mixture was stirred at 20°C for 25 min and then concentrated under vacuum. The oily residue was kept at 60°C under vacuum for 25 min and then distilled, b.p. 120°C/0.05 Torr to give **7b** of 340 mg (99%). ^{31}P NMR (81 MHz, C_6D_6): $\delta = 134.1$ ppm; ^1H NMR (300 MHz, C6D6): $\delta = 1.30$ (d, $J = 5.4$ Hz, 12 H, CH_3), 2.16 + 2.18 (2^xs, 9 H, CH_3), 4.03 (br s, 2 H, CH), 6.78 (s, 2 H, CH) ppm; ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 18.6$ (d, $J = 2.5$ Hz, CH_3), 19.8 (s, CH_3), 20.2 (s, CH_3), 48.6 (s, CH), 125.0 (s, i-C), 128.3 (s, CH), 131.2 (s, i-C), 143.6 (d, $J = 30$ Hz, i-C), 154.1 (d, $J = 99$ Hz, C=N); elemental analysis calcd (%) for $C_{16}H_{25}Cl_2N_2P$ (347.27): Cl 20.42, P 8.92; found: Cl 20.06, P 9.05.

Dichlorophosphoranide (**9**): To a solution of silylformamidine **8** (1.0 g, 4.5 mmol) and **1** (670 mg, 4.5 mmol) in CH_2Cl_2 (10 mL), cooled to freezing, PCl_3 (730 mg, 5.3 mmol) was added. The reaction mixture was allowed to warm at ambient temperature (16°C) with stirring. The solvent was removed under vacuum. The residue was extracted with Et_2O (15 mL). The insoluble powder was filtered under argon, washed with Et_2O (3 × 10 mL), and dried under vacuum. The collected solid was shaken in THF (26 mL), insoluble part was collected by filtration and washed with THF (5 mL), and the filtrate was evaporated under vacuum. The residue was recrystallized from CH_3CN (7 mL) to give **9** of 330 mg (18%). M.p. 141–144°C (decomp); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 124.7$ ppm. ^1H NMR (500 MHz, C_6D_6): $\delta = 1.23$ (br s, 6 H, CH_3), 2.49 (br s, 6 H, CH_3), 4.67 (br s, 1 H, CH), 7.07 (br s, 6 H, Ph), 8.26 (br s, 4 H, Ph). Elemental analysis calcd (%) for $C_{18}H_{23}Cl_2N_4P$ (397.29): Cl 17.85, P 7.80; found: Cl 18.11, P 7.69.

Chlorophosphine (**10**): To a solution of silylformamidine **4a** (0.96 g, 3.7 mmol) in benzene (2.5 mL), phosphorus trichloride (0.25 g, 1.8 mmol) in benzene (1 mL) was added. A slight exothermic effect was observed. In 1 h, all solvents evaporated to give a white solid. ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 30$ ppm [7].

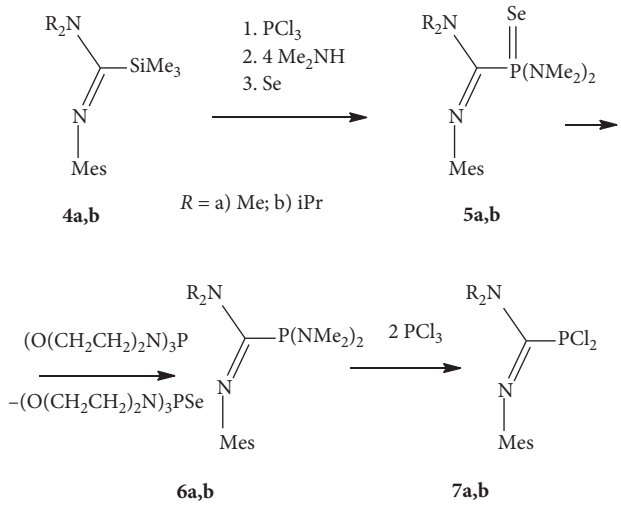
Dichlorophosphoranide (**11**): To a solution of chlorophosphine **10** (0.6 g, 1.4 mmol) in benzene (5 mL), a solution of hydrogen chloride (0.05 g, 1.4 mmol) in ether (3 mL) was added. The precipitated solid was collected by filtration. The solid was washed with ether. The solid was recrystallized from benzene to give white crystals of 0.52 g, 80%. M.p. 181–182°C. ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -102$ ppm; elemental analysis calcd (%) for $C_{24}H_{35}Cl_2N_4P$ (481.45): Cl 14.73, P 6.43; found: Cl 14.38, P 6.04.

3. Results and Discussion

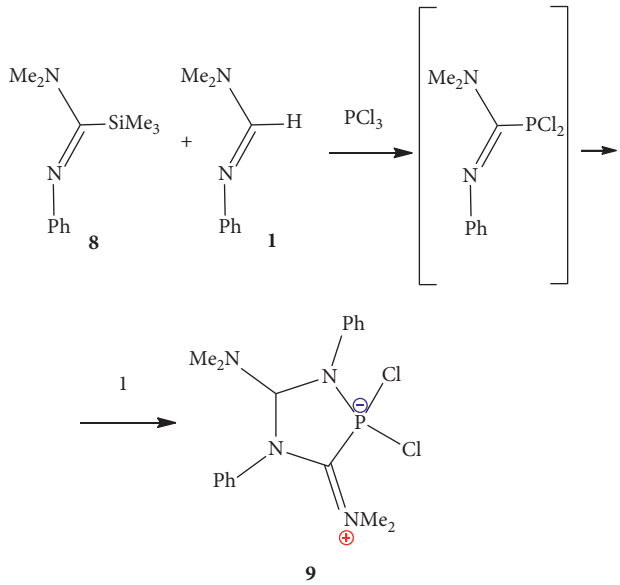
We started the synthesis of derivatives bearing one formamidine substituent. Thus, compounds **4a** and **b** react consecutively with phosphorus trichloride, dimethylamine, and selenium in a one-pot procedure affording stable derivatives **5a** and **b** which were isolated and fully characterized. Phosphineselenides **5a** and **b** were purified by silica gel plate chromatography. Phosphineselenides **5a** and **b** were reduced by tris(morpholino)phosphine to give phosphonous diamides **6a** and **b**. They are stable, distillable in high-vacuum compounds. While the ^{31}P NMR spectrum of highly sterically hindered compound **6b** involves only one signal at 90.1 ppm, compound **6a** exhibits two signals at 92.4 and 88.7 ppm in a ratio 10 : 1 corresponding to syn/anti-isomers. The reaction of phosphonous diamide **6b** with phosphorus trichloride in a 1 : 2 ratio produced dichlorophosphine **7b** ($\delta_p = 134$ ppm), which was isolated by distillation as an individual compound (Scheme 2). The compound is stable in the solid state, but in solution, it decomposes quite promptly, in a few hours. Monitoring this process by ^{31}P NMR reveals formation of numerous signals including phosphorus trichloride. The reaction of phosphonous diamide **6a** under the same conditions also afforded dichlorophosphine **7a**, which cannot be isolated as a pure compound, but it is possible to obtain its derivatives. The method of dichlorophosphine synthesis being available, it was possible to validate the proposed mechanism for the formation of dibromophosphoranide (Scheme 1). It is known that formamidines do not react with phosphorus trichloride. It allowed us to carry out a three-component reaction of formamidine **1**, its trimethylsilylated derivative **8** with phosphorus trichloride. Initially, PCl_3 would react with silylated formamidine **8** to form the corresponding dichlorophosphine, which, according to the proposed mechanism, should react with formamidine **1** to form dichlorophosphoranide **9** in the next stage (Scheme 3).

Indeed, by adding phosphorus trichloride to a mixture of formamidine **1** and its silylated derivative **8**, the target dichlorophosphoranide **9** was prepared. The reaction mixture was monitored by ^{31}P NMR spectroscopy, and it exhibited only one ^{31}P NMR signal at 124 ppm. Nevertheless, we separated phosphoranide **9** only during 18% yield. Its structure was confirmed by X-ray diffractometry. Compound **9** crystallizes in the space group P^{-1} with 2 molecules in the unit cell. Figure 2 shows the molecular structure and contains key interatomic distances and bond angles.

The molecular structure of **9** shows a distorted, ψ-trigonal bipyramidal coordination of the P atom. Two chlorine atoms occupy the axial positions, while a lone electron pair and the cycle are located in the equatorial positions. The P–Cl bond lengths in dichlorophosphoranide **9** are very different (P1–Cl1 2.8509(6) Å; P1–Cl2 2.2058(6) Å). The second value is close to P–Cl bond lengths ranging from 2.295 to 2.469 Å in related phosphorus compounds, and the first value is far beyond that range and is intermediate between the covalent P–Cl bond and cationic-anionic distances in crystals [4, 10]. In comparison, the P–Br bond lengths in dibromophosphoranide **3** are very similar in length: 2.6945(16) and 2.5792(15) Å. Other structural



Scheme 2: Synthesis of dichlorophosphines and their derivatives.



Scheme 3: Synthesis of dichlorophosphoranide **9**.

parameters of both phosphoranides **3** and **9** are quite close. ^{31}P NMR chemical shifts of phosphoranide **3** ($\delta_p = 56.8$ ppm in $CDCl_3$) and **9** ($\delta_p = 124.7$ ppm in $CDCl_3$) are indicative of their phosphoranide structures. While a high-field shift of phosphoranide **3** testifies that in a solution, it does not dissociate, a low-field shift of phosphoranide **9** attests to a high degree of dissociation. An analogous acyclic dichlorophosphoranide ($\delta_p = 92.3$ ppm in $CDCl_3$) was prepared by addition of 2,2,6,6-tetramethylpiperidinedichlorophosphine to cyclic (alkyl)(amino)carbene. Although X-ray was not available, it was presented as a phosphonium salt [11].

In our previous work, we have shown that silylformamidine **4a** reacts with phosphorus trichloride in a 2 : 1 ratio producing chlorophosphine **10** [7].

Monitoring by ^{31}P NMR, a solution of chlorophosphine **10** ($\delta_p = 31$ ppm) showed that its signal gradually disappears and a signal in a strong field ($\delta_p = -102$ ppm) grows, which became

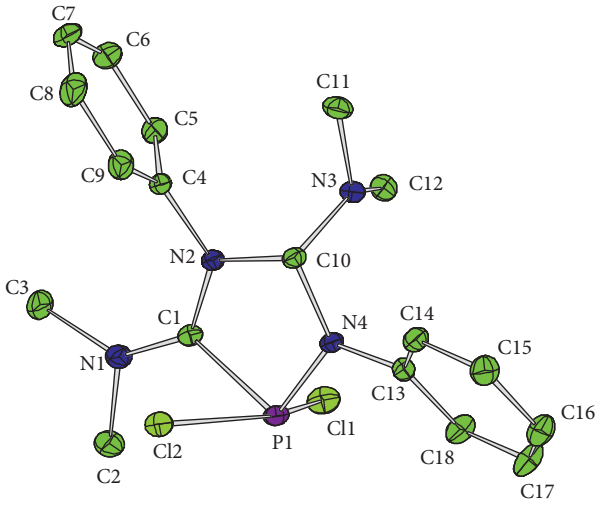
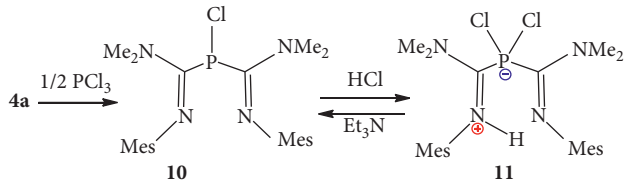


Figure 2: The perspective view of the molecule **9** with 50% probability ellipsoids for non-H-atoms. The selected bond lengths (Å) and angles (°): Cl(1)–P(1) 2.2058(6), Cl(2)–P(1) 2.8509(6), P(1)–N(4) 1.6621(13), P(1)–C(1) 1.8501(15), N(1)–C(1) 1.313(2), N(2)–C(1) 1.3255(19), N(2)–C(10) 1.5135(18), N(3)–C(10) 1.4115(19), N(4)–C(10) 1.4624(19); N(4)P(1)C(1) 89.10(7), P(1)C(1)N(2) 110.67(11), C(1)N(2)C(10) 116.88(12), N(2)C(10)N(4) 103.16(11), P(1)N(4)C(1).119.37(10).



Scheme 4: Synthesis of dichlorophosphoranide **11**.

predominant over time. When triethylamine was added to the solution, the signal ($\delta_p = -102$ ppm) disappeared and the signal of chlorophosphine **10** was restored. We carried out a quantitative experiment in which an equivalent amount of hydrogen chloride was added to a solution of chlorophosphine **10**. It transformed into dichlorophosphoranide **11**(Scheme 4). The reaction is reversible and, when triethylamine is added, phosphoranide **11** is converted to chlorophosphine **10**. The molecular structure of phosphoranide **11** was unambiguously determined by single-crystal X-ray diffractometry (Figure 3). Compound **11** crystallizes in the Pna21 space group with 4 molecules in the unit cell. Figure 3 shows that the molecular structure contains some interatomic distances and bond angles. The molecular structure of phosphoranide **11** shows that P–Cl bond lengths are almost the same (Cl(1)–P(1) 2.3444(9), Cl(2)–P(1) 2.3303(9) Å). The ^{31}P resonance of **11** ($\delta_p = -102$ ppm in $CDCl_3$) is substantially shifted to a higher field, but it is very close to that of the related phosphoranide **C** ($\delta_p = -98.9$ ppm in CD_2Cl_2). Such a substantial highfield shift correlates with a smaller degree of dissociation into phosphine and hydrogen chloride [12, 13]. CCDC 1938108 (**9**) and 1938107 (**11**) contain the supplementary crystallographic data for this paper.

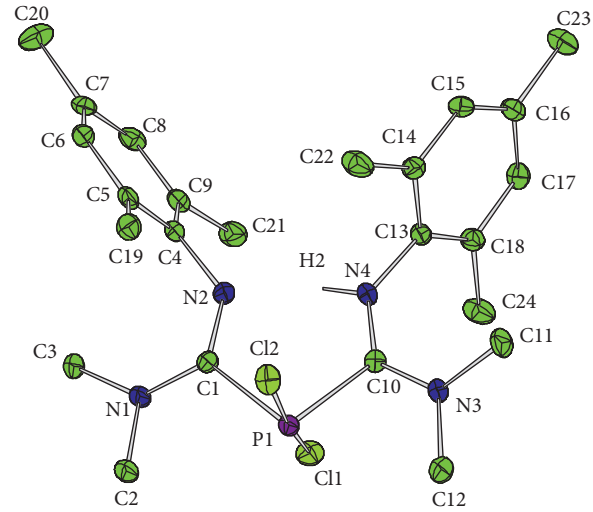


Figure 3: The perspective view of the molecule **11** with 50% probability ellipsoids for non-H-atoms. The selected bond lengths (Å) and angles (°): Cl(1)–P(1) 2.3444(9), Cl(2)–P(1) 2.3303(9), P(1)–C(1) 1.893(2), P(1)–C(10) 1.887(2), N(1)–C(1) 1.331(3), N(2)–C(1) 1.296(3), N(3)–C(10) 1.342(3), N(4)–C(10) 1.292(3); C(1)P(1)C(10) 103.99(10), N(1)C(1)N(2) 128.2(2), N(3)C(10)N(4) 127.4(2).

4. Conclusions

We confirmed experimentally the mechanism for formation of dichloro(dibromo)-phosphoranides **3** and **9** previously proposed on the basis of DFT calculations. Dichlorophosphoranide **9** was prepared by a three-component reaction between *C*-trimethylsilyl-*N*,*N*-dimethyl-*N*′-phenylformamidine, *N*,*N*-dimethyl-*N*′-phenylformamidine, and phosphorus trichloride. At first, *C*-trimethylsilyl-*N*,*N*-dimethyl-*N*′-phenylformamidine reacts with phosphorus trichloride to give the corresponding dichlorophosphine bearing the formamidine substituent, followed by addition of *N*,*N*-dimethyl-*N*′-phenylformamidine to afford the target dichlorophosphoranide **9**. It was shown that chlorophosphine **10** reacts with hydrogen chloride to form dichlorophosphoranide **11**. In the presence of triethylamine, the reaction is reversible and gives chlorophosphine **10**. The molecular structures of phosphoranides **9** and **11** were determined by single-crystal X-ray diffractometry.

Data Availability

The ^{1}H, ^{13}C, ^{31}P NMR instrumental data and elemental analysis data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

The supplementary materials contain copies of ^{1}H and ^{13}C NMR spectra. (*Supplementary Materials*)

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