

MesPX₂/IsPX₂ as Precursors for the Preparation of Phosphasilenes

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The one-pot reaction of L¹SiCl (L¹=PhC(NtBu)₂) with MesPX₂/ IsPX₂ (X=Cl, Br; Is=2,4,6-*i*Pr₃C₆H₂, Mes=2,4,6-Me₃C₆H₂) in the presence of KC₈ yielded two phosphasilene compounds L¹Si (Cl)=Pls (1) and L¹Si(Cl)=PMes (2) with interesting Cl–Si=P characteristics. The introduction of Cl–Si=P moiety improved the reactivity of phosphasilene. Furthermore, phosphasilenes 1 and 2 with LSi as well as Si=P building units are sensitive to moisture with distinct differences. The hydrolysis of 2 resulted in two products [L¹(PHMes)Si]₂(μ -O)₂ (3) and L¹Cl (4), respectively, due to the amount of water, while the hydrolysis of 1 afforded L¹Cl (4). In addition to the silylene L¹SiCl, different types of aluminum compounds were studied to react with IsPX₂/MesPX₂ in the presence of KC₈ in THF at low temperature. However, we failed to isolate the desired compounds due to the formation of numerous by-products.

Introduction

Compounds featuring heteroleptic multiple bonds between heavier main-group elements have attracted considerable attention in recent years according to their application in the synthesis of novel organometallic compounds.^[1] Among them, phosphasilenes with a Si=P bond made great progress.^[1a,b,2] The Si=P bond is slightly polarized due to the small difference in electronegativity values between silicon and phosphorus (Si 1.9 and P 2.1). One reason for further shortening of the Si–P bond distance is certainly due to the Si⁺–P⁻ polarization. The direction and degree of the polarization can readily be modulated by the polarity of substituents along with the coordination number of the Si and P atoms. Since the first synthesis of phosphasilene by Bickelhaupt et al.^[3] (Figure 1, I) various compounds containing the Si=P motif have been

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- Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202000966
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Figure 1. Examples of phosphasilenes with various functional groups at silicon and phosphorus.

obtained and characterized during the last three decades.^[2] Notably, Driess and co-workers contributed significantly to the synthesis of various phosphasilenes when they introduced the P-silyl-substituted phosphasilenes in 1991.^[4] Generally, compounds with Si=P bonds are stabilized using alkyl/aryl (e.g. I, Figure 1),^[5] silyl (e.g. II, Figure 1)^[6] and phosphorus substituents^[7] or alternatively bulky ligands^[8] (e.g. III, IV, Figure 1) on the Si or P atom. β -Elimination reaction was the preferred synthetic route for preparing phosphasilenes. In addition, some Si=P species also could be obtained from stable silylene precursors through "1,2-H shift" of coordinated NHC \rightarrow $(R^{1})Si-P(H)R^{2[9]}$ (e.g. V, Figure 1) or through 1,2-silyl migration of $LSi-P(SiMe_3)_2$ (L = PhC(NtBu)₂)^[8b,10] (VI, Figure 1). In addition, Inoue et al.^[11b] and our group^[11a,c] contribute to the current synthetic protocol for preparing phosphasilenes. Furthermore, the metallophosphasilenes VII^[6a] and VIII^[12] were derived from substitution of a hydrogen atom at phosphorus with ZnMe or : PbL^2 ($L^2 = HC(CMeNAr)_2$, $Ar = 2,6 - iPr_2C_6H_3$). Moreover, it was shown, that AuCl coordinates to phosphorus of Si=P with a



lone pair of electrons to give a stable transition-metal complex (e.g. $\boldsymbol{IX})^{[13]}$

Phosphinidenes are recognized as short-lived intermediates. Recently, carbene-stabilized phosphinidenes with two lone pairs of electrons at one P atom have attracted great research interest. They are considered as ligands comparable to carbones.^[14] In addition, carbene-stabilized phosphinidenes are important intermediates for the synthesis of novel products.^[15] Reduction of bis(trichlorosilyl)phosphane (IsPCl₂, Is=2,4,6*i*Pr₃C₆H₂) with KC₈ in the presence of carbene resulted in the formation of phosphasilene X and XI, respectively, with chlorine functions at the silicon atom (Figure 1).^[15a] In this reaction IsPCl₂ was the precursor for short-lived intermediate phosphinidene (IsP) and SiCl₂, respectively. Obviously, the intermediates were trapped to form products X and XI in the presence of carbene. This suggests that phosphinidenes could be trapped by silicon carbene to give the corresponding phosphasilenes. Other than the mentioned examples of phosphasilenes is the congener with the Cl-Si=P functional group, which are seldom reported. Herein, we report on a new strategy for the synthesis of phosphasilene L¹Si(CI)=PIs (1) and L¹Si(CI)=PMes (2), respectively. The reaction of MesPX₂/IsPX₂ as the precursor for phosphinidenes (X=Cl, Br) with L¹SiCl (L¹=PhC(NtBu)₂) and KC₈ in a molar ratio of 1:1:2 in tetrahydrofuran (THF) was modified.

Results and Discussion

According to the previous literature, Cl atoms in both L¹SiCl and IsPCl₂ could be reduced by using excess of KC₈ to obtain 1,4diphospha-2,3-disila butadiene derivative with a (-P=Si=Si=P-) chain^[11c] Treatment of IsPX₂ with L¹SiCl and KC₈ in a molar ratio of 1:1:2 in tetrahydrofuran (THF) afforded compound L¹Si (Cl)=Pls (1) (Figure 2) (81 % yield). Cl as well as Br atoms of IsPX₂ (X=Cl or Br) could be reduced during the reaction, probably affording short-lived "phosphinidene" (IsP) in situ. Instantly "IsP" was trapped by LSiCl to form phosphasilene. The result suggests that halogen atoms X (X=Cl, Br) of IsPX₂ were reduced prior to that of L¹SiCl, when the exact amount of KC₈ is given according to the ratio. After the reaction, all volatiles were removed under vacuum and the residue was extracted with nhexane. Compound 1 was isolated after growing orange crystals from a concentrated *n*-hexane solution and characterized by single-crystal X-ray diffraction studies and NMR spectroscopy. The X-ray single crystal structure shows that 1 crystallizes in the triclinic space group P1 and exhibits a Si(CI)=P framework. The Si(1)=P(1) bond length of 2.1031(10) Å exhibits double bond character when compared with the Si=P bond length of phosphasilene VI (2.095(3) Å)^[10], X (2.1205(9) Å and 2.1225(9) Å) and XI (2.1129(10) Å), respectively^[15a]. The Si(1)–Cl(1) of 2.0606(6) Å is slightly shorter than the Si-Cl bond (2.156(1) Å) of L¹SiCl.^[16] The ¹H NMR spectrum of **1** is in agreement with the single-crystal structure with resonances at δ 1.60 (o-*i*Pr₂), δ 1.32 (*p*-*i*Pr) and δ 1.07 (*t*Bu) in a ratio of 2:1:3. The ³¹P NMR shifts are found in the range (δ 164.79, δ 159.39 and δ 151.88) for IsPX₂ at δ –185.76. Furthermore, the reaction of MesPX₂ with L¹SiCl and KC_8 resulted in the formation of L¹Si(CI)=PMes (2) (Figure 3) in 69% yield under optimized conditions. X-ray quality single crystals of 2 were obtained in *n*-hexane solution at low temperature. Compound 2 crystallizes in the monoclinic space group $P2_1/n$ containing the Si(Cl)=P moiety. The bond length of Si(1)=P(1) (2.1016(7) Å) and Si(1)-Cl(1) (2.0725(7) Å) are close to those bonds of L¹Si(Cl)=PIs (1). The singlet resonances δ 2.66 (o- $C_6H_2Me_2$), $\delta 2.20$ (p- C_6H_2Me), $\delta 1.20$ (tBu) in the ¹H NMR spectrum with the ratio of 2:1:6 and δ –171.31 in ³¹P NMR spectrum confirms the structure of **2**. In the ²⁹Si NMR spectrum, both compounds 1 (δ 6.69, d, J=213.84) and 2 (δ 8.50, d, J= 212.85) display double resonances. The synthesis of 1 and 2 are shown in Scheme 1.

Phosphasilenes L¹Si(Cl)=PIs (1) and L¹Si(Cl)=PMes (2) are sensitive to moisture and easily decompose at open air. Treatment of 2 in THF-d8 in the presence of small amounts of water resulted in the hydrolyzed product $[L^1(PHMes)Si]_2(\mu-O)_2$ (3) (Figure 4). X-ray-quality single crystals of 3 were obtained in THF-d8. 3 crystallizes in the triclinic space group $P\overline{1}$. The structure consists of a rectangular cyclodisiloxane Si₂O₂ ring orthogonal to a slightly distorted planar skeleton containing the silicon atoms and their pendant nitrogen atoms. The Si–P



Figure 2. X-ray single-crystal structure of 1 Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–P1 2.1031(10), Si1–Cl1 2.0606(6), Si1–N1 1.8471(13), Si1–N2 1.8097(13), P1–Si1–N1 123.57(4), P1–Si1–Cl1 120.69(3), P1–Si1–N2 117.14(5), N1–Si1–N2 71.69(6), N1–Si1–Cl1 104.05(4), N2–Si1–Cl1 109.46(5), Si1–P1–C16 102.74(5).



Figure 3. X-ray single-crystal structure of 2. Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–P1 2.1016(7), Si1–Cl1 2.0725(7), Si1–N1 1.8139(12), Si1–N2 1.8380(13), P1–Si1–N1 114.35(4), P1–Si1–Cl1 122.15(3), P1–Si1–N2 125.40(5), N1–Si1–N2 71.89(5), ofN1–Si1–Cl1 110.53(5), N2–Si1–Cl1 101.77(4).





Scheme 1. Synthesis of compounds 1 and 2 with characteristic Si(Cl)=P feature.



Figure 4. X-ray single-crystal structure of **3.** Anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–O1 1.6804(15), Si1–O1 A 1.7205(13), Si1–P1 2.2744(13), N1–Si1–N2 68.77(7), Si1–O1–SiA 94.95(7), O1–Si1–O1 A 85.05(7), Si1–P1–C16 108.34(7).

bond of 2.2744(13) Å is longer when compared with the double bond of 2 (2.1016(7) Å), exhibiting a single covalent bond. In addition, the structure of 3 is also confirmed by NMR spectra of the mixture of 2. In the ¹H NMR spectrum, a selection of proton singlet resonances of o-C₆H₂Me₂, p-C₆H₂Me and tBu (δ 2.60, 2.25, 1.26) are only slightly changed, when compared with the corresponding resonances (δ 2.66, 2.20, 1.20) of compound 2. There is a new proton resonance at δ –122.21 in the ³¹P(H) NMR spectrum and two new resonances at δ –80.29, –81.65 in the ²⁹Si NMR spectrum, which is comparable with those of compound [L¹(PCHPh₂)Si]₂(μ -O)₂.^[17]

Furthermore, the stoichiometric reactions of 1 or 2 with 1 equiv. amounts of H_2O are studied. We failed to obtain the desired compounds $[L^1(PHIs)Si]_2(\mu-O)_2$ and $[L^1(PHMes)Si]_2(\mu-O)_2$. Both compounds 1 and 2 decompose under cleavage of the L¹ and Si fragment giving the decomposition product L¹·HCI (4) (see Figure S1 in SI) with Si and P fragments. Compound 4 was obtained after growing colorless crystals from the resulting solution (including Si and P fragments) and characterized by single-crystal X-ray diffraction studies and ¹H NMR spectroscopy. The structure of 4 exhibits an L¹H skeleton and a CI atom. The

¹H NMR spectrum exhibits the L¹H structure. We propose that the hydrolysis of **2** resulted in $[L^1(PHMes)Si]_2(\mu-O)_2$ which is extremely sensitive and depends on the condition and amount of H₂O. When traces of water are added to compound **2** a shortlived intermediate **3 A** might be formed. (Scheme 2) Then its dimerization afforded the desired product $[L^1(PHMes)Si]_2(\mu-O)_2$ (**3**) with the elimination of 2 equiv. of HCI. (see Scheme 2) In the stoichiometric amount of H₂O used, the decomposition resulted in the formation **4** together with uncharacterized Si and P species.

In addition to the silylene L¹SiCl, aluminum compounds (LiAlH₄, H₃Al·NEtMe₂ and AlMe₃, respectively) are explored to react with IsPX₂/MesPX₂ in the presence of KC₈ in THF at low temperature. However, we failed to obtain the desired compounds due to low reactivity of aluminum compounds or the formation of by-products.

Conclusion

The one-pot reaction of L¹SiCl with MesPX₂/IsPX₂ in the presence of KC₈ yielded two phosphasilene compounds L¹Si (Cl)=PIs (1) and L¹Si(Cl)=PMes (2), each with the Cl–Si=P moiety. In addition, the reaction of 1 and 2, respectively, with water, was explored. Due to different amounts and conditions of adding H₂O, the hydrolysis of 2 resulted in two hydrolyzed products [L¹(PHMes)Si]₂(μ -O)₂ (3) and L¹·HCI (4) with Si and P fragments, respectively.

Experimental Section

General procedures

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or glovebox techniques. All solvents were refluxed over sodium/potassium alloy under a nitrogen atmosphere and distilled prior to use. Commercially available chemicals were purchased from Sigma Aldrich or Alfa



Scheme 2. Hydrolysis of 2 resulted in products 3 and 4, respectively.



Aesar, and used as received. Solution NMR spectra were recorded on Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvents C_6D_6 and THF-D8 were dried by stirring for 2 days over Na/K alloy followed by distillation in a vacuum and degassed. Elemental analysis was performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus. IsPX₂/MesPX₂ (X=Br or Cl)^[8c,19] and L¹SiCl (PhC(NtBu)₂)^[20] were synthesized according to the literature.

Synthesis of L¹Si(CI)=PIs (1)

L¹SiCl (L¹=PhC(NtBu)₂) (294 mg, 1.0 mmol), IsPX₂ (Is=2,4,6-iPr₃C₆H₂) (350 mg, 1.0 mmol, determined by ¹H NMR) and KC_8 (270 mg, 2.0 mmol) were placed in a 100 mL round-bottomed flask and 20 mL of THF was added to the mixture at -78 °C. The reaction was allowed to warm up to room temperature and was stirred overnight giving an orange-red solution. Then the volatiles was removed under vacuum and the residue was extracted with 50 mL of nhexane. After filtration, the concentrated filtrate was stored at -26 °C in a deep freezer. Orange crystals of 1 were obtained from n-hexane after two days. Total yield: 0.428 g (81%). Mp: 148.8-151.3 °C (decomposition). ¹H NMR (300 MHz, C_6D_6): δ 7.29 (d, J = 1.9 Hz, 2H), 6.90-6.61 (m, 5H, Ph-H), 5.14-4.96 (m, 2H, CH), 2.92 (hept, J = 6.9 Hz, 1H, CH), 1.60 (d, J = 6.9 Hz, 12H, o-iPr₂), 1.32 (d, J =6.9 Hz, 6H, p-iPr), 1.07 (s, 18H, tBu). ¹³C NMR (75 MHz, C_eD_e): δ 175.74 (s), 155.50 (d, J=6.8 Hz), 146.14 (s), 132.24 (s), 131.52 (s), 130.22 (s), 129.69 (s), 120.40 (s), 55.12 (s), 34.52 (d, J=8.8 Hz), 31.59 (s), 30.63 (d, J = 1.7 Hz), 24.26 (d, J = 10.5 Hz), 22.68 (s). ³¹P NMR (121 MHz, THF): δ –185.76 (s). ²⁹Si NMR (99 MHz, C₆D₆): δ 6.69 (d, J = 213.84). Elemental analysis found in % (calcd) for $C_{30}H_{46}CIN_2PSi$ (528.29): C, 68.09; H, 8.76; N, 5.29. Found C, 67.43; H, 9.02; N, 5.26.

Synthesis of L¹Si(Cl)=PMes (2)

 $L^{1}SiCl$ ($L^{1}=PhC(NtBu)_{2}$) (294 mg, 1.0 mmol) and KC₈ (270 mg, 2.0 mmol) were placed in a 100 mL round-bottomed flask and 20 mL of THF was added. The solution of MesPX₂ (Mes=2,4,6- $Me_{3}C_{6}H_{2}$) (250 mg, 1.0 mmol, determined by ¹H NMR) in THF (10 mL) was added to this mixture at -78 °C. The reaction was allowed to warm up to room temperature and was stirred overnight giving an orange solution. Then the volatiles was removed under vacuum and the residue was extracted with 50 mL of *n*-hexane. After filtration, the concentrated filtrate was stored at -26 °C in a deep freezer. Orange crystals of 2 was obtained from n-hexane after three days. Total yield: 0.307 g (69%). Mp: 143.1-145.4 °C (decomposition). ¹H NMR (300 MHz, THF-d8): δ 7.64–7.52 (m, 5H, Ph–H), 6.84 (s, 2H, H–Mes), 2.66 (s, 6H, o-C₆H₂Me₂), 2.20 (s, 3H, p-C₆H₂Me), 1.20 (s, 18H, tBu). ¹³C NMR (75 MHz, THF-d8): δ 176.37 (s), 144.48 (d, J = 8.2 Hz), 133.07 (s), 131.00 (s), 129.70 (s), 128.40 (s), 128.23 (d, J =3.75), 127.67 (s), 127.25 (s), 55.28 (s), 30.12 (s), 25.90 (d, J=10.6 Hz), 20.08 (s). $^{\rm 31}{\rm P}$ NMR (121 MHz, THF-d8): δ –171.31 (s). $^{\rm 29}{\rm Si}$ NMR (99 MHz, C₆D₆): δ 8.50 (d, J=212.85). Elemental analysis found in % (calcd) for C₂₄H₃₄ClN₂PSi (444.19): C, 64.77; H, 7.70; N, 6.29. Found C, 64.93; H, 7.46; N, 6.54.

Synthesis of $[L^{1}(PHMes)Si]_{2}(\mu-O)_{2}$ (3)

The solution of L¹Si(CI)=PMes (**2**) (30 mg) in 0.5 mL THF-d8 was kept under air condition in a closed NMR tube for two weeks. Compound **2** hydrolyzed to give $[L^1(PHMes)Si]_2(\mu-O)_2$ (**3**). ¹H NMR (300 MHz, THF-d8): δ about 7.65–7.40 (m, 10H, Ph–H), 6.89 (s, 4H, H–Mes), 2.60 (s, 12H, $o-C_6H_2Me$), 2.25 (s, 6H, $p-C_6H_2Me$), 1.26 (s, 36H, *t*Bu). (The NMR detailed data was determined by comparing the

mixture **2** and **3** with **2**.) ³¹P(H) NMR (121 MHz, THF-d8): δ –122.21 (s). ²⁹Si NMR (99 MHz, C₆D₆): δ –80.29 (d, J=30.29), –81.65 (d, J=27.92).

Synthesis of L¹·HCl (4)

L¹Si(CI)=PMes (2) (134 mg, 0.3 mmol) was placed in a 100 mL round-bottomed flask and 6 mL of water containing THF (0.05 M H₂O in THF) were added under stirring. The color of the solution changed from orange to light yellow during the addition of hydrous THF. The reaction was stirred for another hour. The resulting solution was stored at 0 °C in a freezer and colorless needle-like crystals of 4 were obtained from THF overnight. ¹H NMR (300 MHz, C₆D₆): δ 12.21 (s, 2H, NH), 6.91–6.75 (m, 5H, ArH), 0.88 (s, 18H, *t*Bu). The resulting solution and difficult to separate from the mixture.

Crystallographic investigations at 100(2)K

Crystal data for 1: $C_{33}H_{53}CIN_2PSi$, $M_r = 572.28 \text{ g/mol}$, $0.18 \times 0.14 \times$ 0.08 mm, triclinic, $P\overline{1}$, a = 10.113(2) Å, b = 10.128(2) Å, c =18.897(3) Å, $\alpha = 91.93(2)^{\circ}$; $\beta = 102.43(2)^{\circ}$, $\gamma = 114.53(3)^{\circ}$, V = 1703.0(7) Å³, Z = 2, μ (Mo K_a) = 0.217 mm⁻¹, $\theta_{max} = 26.4^{\circ}$, 46767 reflections measured, 6971 independent ($R_{int} = 0.0376$), $R_1 = 0.0308$ $[l > 2\sigma(l)], wR_2 = 0.0774$ (all data), res. density peaks: 0.327/ -0.227 eA⁻³, CCDC: 2036269. Crystal data for **2**: $C_{24}H_{34}CIN_2PSi$, M_r = 445.04 g/mol, $0.17 \times 0.14 \times 0.13$ mm, monoclinic, $P2_1/n$, a =10.436(2) Å, b = 16.422(3) Å, c = 14.647(2) Å, $\beta = 91.59(2)^{\circ}$, V =2509.2(7) Å³, Z=4, μ (Mo K_a)=0.276 mm⁻¹, θ_{max} =26.4°, 50704 reflections measured, 5135 independent ($R_{int} = 0.0319$), $R_1 = 0.0319$ $[I > 2\sigma(I)]$, $wR_2 = 0.0906$ (all data), res. density peaks: 0.334/ -0.213 eA⁻³, CCDC: 2036270. Crystal data for **3**: $C_{28}H_{43}N_2O_2PSi$, $M_r =$ 498.70 g/mol, $0.20 \times 0.14 \times 0.11$ mm, triclinic, P1, a = 10.770(4) Å, b =11.391(4) Å, c = 13.241(5) Å, $\alpha = 100.65(2)^{\circ}$; $\beta = 110.14(3)^{\circ}$, $\gamma =$ 107.09(2)°, $V = 1381.7(9) \text{ Å}^3$, Z = 2, μ (Mo K_a) = 0.170 mm⁻¹, $\theta_{max} =$ 26.4°, 26795 reflections measured, 5677 independent ($R_{int} = 0.0361$), $R_1 = 0.0425$ [*I* > 2 σ (I)], $wR_2 = 0.1190$ (all data), res. density peaks: $0.420/-0.252 \text{ eA}^{-3}$, CCDC: 2036271. Crystal data for 4: $C_{15}H_{25}CIN_{27}$ $M_r = 268.82 \text{ g/mol}, 0.48 \times 0.20 \times 0.18 \text{ mm}, \text{ trigonal}, R\overline{3}, a = b =$ 36.463(3) Å, c = 6.679(2) Å, V = 7690(3) Å³, Z = 18, μ (Mo K_a) = 0.212 mm⁻¹, $\theta_{max} = 26.4^{\circ}$, 39466 reflections measured, 3507 independent ($R_{int} = 0.0502$), $R_1 = 0.0329$ [$I > 2\sigma(I)$], $wR_2 = 0.0811$ (all data), res. density peaks: 0.270/-0.194 eA⁻³, CCDC: 2036272. Shockcooled crystals were selected from a Schlenk flask under argon atmosphere using the X-TEMP2 device.^[21,22] Data were collected with a Mo–lµS microfocus source $^{\scriptscriptstyle [23]}$ and integrated with SAINT. $^{\scriptscriptstyle [24]}$ A multi-scan absorption correction was applied using SADABS.^[25] The structures were solved by SHELXT^[26] and refined on F² using SHELXL^[27] in the graphical user interface ShelXle.^[28] For diffuse residual density in a solvent channel in 4, the SQUEEZE routine in PLATON was used.^[29]

Deposition Numbers 2036269 (for 1), 2036270 (for 2), 2036271 (for 3), and 2036272 (for 4) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.a-c.uk/structures.

Acknowledgements

H. W. R. thanks the DFG for support of this work (RO 224/71-1). D. S. thanks the Danish National Research Foundation (DNRF93)



funded Center for Materials Crystallography (CMC) for partial support. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Reduction · Phosphorus · Silicon · Phosphinidenes · Phosphasilanes · Structure elucidation

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Manuscript received: October 17, 2020 Revised manuscript received: November 25, 2020 Accepted manuscript online: November 28, 2020