■ **Phosphorus Silicon Compounds**

Phosphorus Silicon Compounds from the Reduction of MesP(H)SiCl₂Ph/Carbene with and without Metal

Yashuai Liu,[a,b] Helena Keil,[a] Zhi Yang,*[b] Regine Herbst-Irmer,[a] Herbert W. Roesky,*[a] and Dietmar Stalke*[a]

Dedicated to Prof. Manfred Scheer on the occasion of his 65th birthday

Abstract: MesP(H)SiCl₂Ph (Mes = 2,4,6-Me₃C₆H₂) (**7**) with a reactive Si–Cl and P–H bond can easily be reduced by KC₈ or alternatively by a carbene to give remarkable phosphorus silicon compounds. **7** is readily synthesized from the reaction of MesPH₂ sequentially with *n*BuLi and PhSiCl₃ in a 1:1:1 ratio. KC₈ reduction of MesP(H)SiCl₂Ph (**7**) in the presence of cyclic alkyl(amino) carbene (cAAC^Me) gives (MesPH)₃SiPh (**8**) and cAAC-stabilized Si₂Ph₂ (**9**). In addition, **9** might also be formed

by the reduction of PhSiCl₃ using KC₈ in the presence of cAAC^Me. Treatment of MesP(H)SiCl₂Ph (**7**) with I*i*Pr₂Me₂ (I*i*Pr₂Me₂ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) in a molar ratio of 1:2 results in HCl elimination as I*i*Pr₂Me₂·HCl. The second equivalent of I*i*Pr₂Me₂ was used to yield well-defined phosphasilene (**10**) containing a Ph(Cl)Si=PMes moiety. This unit will gain much application in ligand design because the chlorine atom can readily be replaced by other substituents.

Introduction

During half a century phosphorus silicon compounds have emerged as research hotspots in literature.[1] Silylphosphanes with Si–P bond are important intermediates for further synthesis of phosphorus silicon compounds with various functional groups.[1,2] These compounds are traditionally synthesized via the reaction of polar Si- and P-compounds with salt elimination. Over the last three decades phosphasilenes with Si=P bond have attracted attention of chemists, and various synthetic routes for the preparation of phosphasilenes are reported.[2] Numerous phosphasilenes were obtained from silylphosphanes and its derivatives via the β-elimination reactions described by Bickelhaupt,[3] M. Driess,[4] E. Niecke,[5] K. Tamao[6] et al.[7–10] The majority of phosphasilenes are derived from deprotonation of corresponding silylphosphanes or phosphanides.[3–8] Moreover, a convenient and mild approach to NHC–phosphasilene complexes were obtained via the reaction of halogenosilyl-

substituted secondary phosphanes and two equivalents of NHCs with elimination of NHCs hydrochlorides.[9,10] Furthermore, M. Driess,[11] R. Corriu,[12] A. Baceiredo,[13] C. Cui,[14] D. Scheschkewitz,[15] and S. Inoue[16] developed other synthetic routes for the preparation of phosphasilenes. A selection of phosphasilenes **1–5** are shown in Figure 1. In addition, the reduction of silylphosphanes with Si–P bond resulted in the formation of radicals, carbene-stabilized molecules or compounds with phosphorus silicon multiple bonds. Our group reported on the synthetic route for carbine-stabilized silylene-phosphinidenes[17] and stable radicals [Ph₂PSi(cAAC•)Cl₂][18] via the reaction of cAAC with corresponding phosphorus silicon compounds in the presence of KC₈.
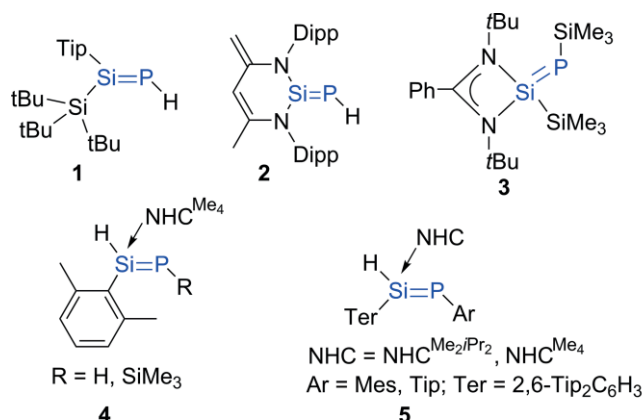
Figure 1. Some typical phosphasilenes **1** to **5**.

[a] Y. Liu, H. Keil, Dr. R. Herbst-Irmer, Prof. H. W. Roesky, Prof. D. Stalke
     Institute of Inorganic Chemistry, University of Göttingen,
     Tammannstrasse 4, 37077 Göttingen, Germany
     E-mail: hroesky@gwdg.de
               dstalke@chemie.uni-goettingen.de
[b] Y. Liu, Prof. Z. Yang
     School of Chemistry and Chemical Engineering, Beijing Institute of
     Technology,
     Beijing 102488, P. R. China
   E-mail: zhiyang@bit.edu.cn

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Silylenes and phosphasilenes have received great interest in research. Therefore, we were searching for a new synthetic route to understand the mechanism of the formation and stability of the products. The syntheses of cyclic alkyl(amino) carbenes (cAACs) were reported in 2005 by Bertrand et al.[19] One σ-withdrawing and π-donating nitrogen atom of a NHC molecule is replaced by a σ-donating quaternary carbon atom in cAAC leading to a lower lying LUMO. cAACs are superior ligands for the stabilization of various unstable chemical species,[20] radicals,[21] and elements in different oxidation states[22] due to their stronger π-accepting properties (Scheme 1). Based on these results, the reduction of MesP(H)SiPhCl$_2$ (**7**) with cAAC^{Me} in the presence of KC$_8$ was explored to yield the corresponding phosphasilenes. However, this reaction failed to give the desired product, instead the unexpected products (MesPH)$_3$SiPh (**8**) and (cAAC^{Me})$_2$Si$_2$Ph$_2$ (**9**) were formed (Scheme 2). Moreover, the formation of **9** is completely different from the synthesis of a series of cyclic alkyl(amino) carbine-stabilized (cAAC:)SiR–SiR(cAAC:) compounds (**6**). The latter compounds were prepared via the reaction of cAAC with RSiCl$_3$ in the presence of 6 equiv. of KC$_8$ (R = H, Me)[23,24] or alternatively by reduction of cAAC → SiCl$_4$ with 6 equiv. of KC$_8$,[25] shown in Scheme 1. Furthermore, a well-defined phosphasilene (**10**) with Cl–Si=P feature was obtained from the reaction of MesP(H)SiPhCl$_2$ with IiPr$_2$Me$_2$.
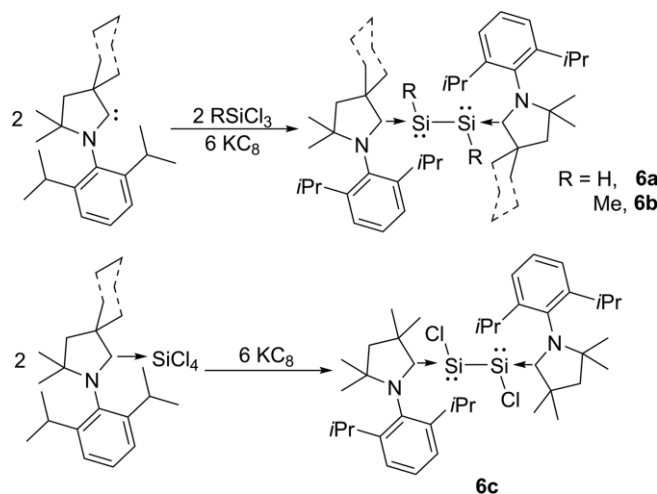
Scheme 1. The synthesis of (cAAC:)$_2$Si$_2$R$_2$.[23–25]
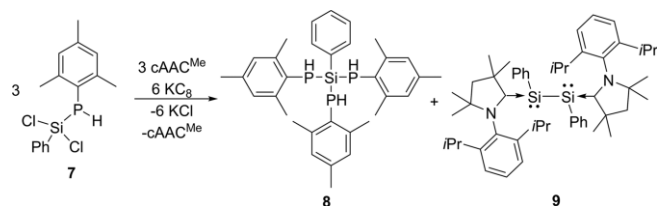
Scheme 2. The formation of (MesPH)$_3$SiPh (**8**) from MesP(H)SiPhCl$_2$ (**7**).

Results and Discussion

Precursor **7** was synthesized as colorless liquid from the reaction of MesPH$_2$ sequentially with nBuLi and PhSiCl$_3$ in a ratio of 1:1:1. It was characterized by NMR spectroscopy. Compound **7** could not be obtained completely pure but contains a small amount of MesPH$_2$ and PhSiCl$_3$. The ^{1}H NMR determined yield was about 70 %. We failed to get pure product **7** by optimizing the synthetic route and purification of precursor **7** by distillation was not possible due to its high boiling point under decomposition. The ^{1}H NMR spectrum exhibits new resonances at δ = 2.29 (o-C$_6$H$_2$Me$_2$), δ = 2.25 (p-C$_6$H$_2$Me) when compared with the corresponding resonances of MesPH$_2$ at δ = 2.44 (o-C$_6$H$_2$Me$_2$), δ = 2.35 (p-C$_6$H$_2$Me). The ^{31}P NMR spectrum exhibits a resonance at –145.60 ppm and the ^{29}Si NMR spectrum shows a resonance at 18.58 (d, J = 56.5 Hz). The ^{31}P NMR resonance is comparable with MesP(H)Si(H)(Cl)Ter (Ter = 2,6-Tip$_2$C$_6$H$_3$, Tip = 2,4,6-iPr$_3$C$_6$H$_2$) at –152.4 ppm. The ^{29}Si NMR resonance is shifted to lower field compared with MesP(H)Si(H)(Cl)Ter at –4.9 ppm.[9]

Traditionally, phosphorus silicon compounds with Si–Cl bonds can be reduced by KC$_8$ in the presence of cAAC, resulting in the formation of silicon carbene adducts or radicals.[17,18] Whereas treatment of **7** with cAAC and KC$_8$ in a molar ratio of 1:1:2 in tetrahydrofuran (THF) yielded the compounds (MesPH)$_3$SiPh (**8**) and (cAAC^{Me})$_2$Si$_2$Ph$_2$ (**9**) (Scheme 2). A small amount of **9** may also be formed as a side product due to the reduction of some PhSiCl$_3$ shown as impurity in the starting material.[23,24]

However, we failed to get single crystals of **9** or pure product from the direct reduction of PhSiCl$_3$ in the presence of cAAC^{Me} by KC$_8$. To the best of our knowledge, this is the first time to obtain (cAAC:)$_2$Si$_2$R$_2$ different from the established routes.[23,24] After the reaction all volatiles were removed under vacuum and the residue was extracted with n-hexane. Product **8** was obtained as colorless crystals and was characterized by single-crystal X-ray diffraction studies (see Figure 2) and NMR spectroscopy. The structure of **8** exhibits a "windmill" like shape with three "P-Mes" vanes and one Ph blade at the silicon hub. The bond length of Si–P [2.2749(7) to 2.2829(8)] is close to the P–Si bond length [2.2125(8) and 2.2155(8)] of IsP(SiCl$_3$)$_2$.[17a] The Si–P–C angles are within the range from 98.97(6) ° to 106.13(6) °. A comparison of ^{1}H NMR and ^{31}P NMR of MesPH$_2$ and MesP(H)SiPhCl$_2$ (**7**) confirmed the formation of **8** from the reduction rather than from the original starting compounds. In the ^{1}H NMR spectrum of **8** four singlet resonances appear for different types of Me groups (δ = 2.23, 2.22, 2.27, 2.12) with a ratio of 2:1:3:2. The ^{31}P{H} NMR show a singlet resonance δ = –158.30 (s) shifted to lower field compared with δ = –145.60 of **7**. The data of NMR confirmed the structure of compound **8**.

In addition, the structure of **9** was determined by single-crystal X-ray diffraction studies (see Figure 3). Both Si atoms are trigonal pyramidal coordinated. The torsion angles for PhSiSiPh and cAACSiSicAAC are –70.91(9) ° and –151.13(9) °, respectively. The Si1–Si2 bond length of 2.3061(8) Å is slightly shorter than those in (cAAC^{Me}:)$_2$Si$_2$H$_2$ [2.3336(13) Å][23] and (cAAC^{Me}:)$_2$Si$_2$Me$_2$ [2.3138(11) Å],[24] respectively. Furthermore, the Si–Ph distances of 1.9027(19) Å (C1) and 1.8989(19) Å (C27) are obviously longer than the Si–C: distances of 1.8046(19) Å (C27) and 1.8029(19) Å (C33), suggesting that the latter show some dual donor acceptor bond character. The crystals of **9** are very small and mixed with an excess of cAAC^{Me}. For the single-crystal X-ray

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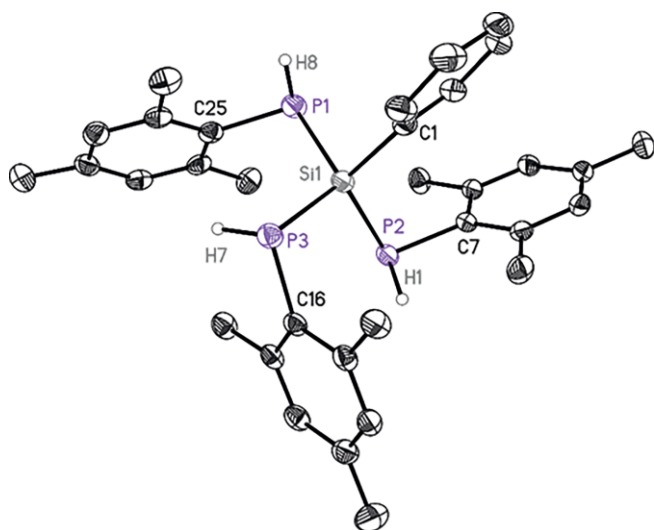European Chemical
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Figure 2. X-ray single-crystal structure of **8**. Anisotropic displacement parameters are depicted at the 50 % probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–P1 2.2749(7), Si1–P2 2.2786(8), Si1–P3 2.2829(8), Si1–C1 1.886(2), P1–Si1–C1 99.35(6), P1–Si1–P2 107.84(3), P1–Si1–P3 114.00(3), P2–Si1–P3 109.13(3), P2–Si1–C1 115.44(6), P3–Si1–C1 110.89(7).

structure analysis, we picked a single crystal from that mixture. The ^{1}H NMR and ^{31}P NMR of the mixture including **9** were measured. However, we failed to get a useful interpretation for compound **9** due to the intricate nature of the spectrum.
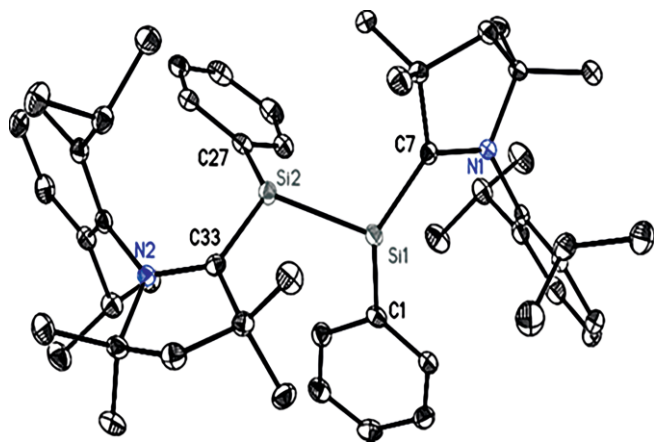

Figure 3. X-ray single-crystal structure of **9**. Anisotropic displacement parameters are depicted at the 50 % probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.3061(8), Si1–C1 1.9027(19), Si1–C7 1.8046(19), Si2–C33 1.8029(19), Si2–C27 1.8989(19), C7–Si1–C1 121.59(8), C1–Si1–Si2 110.72(6), C7–Si1–Si2 110.97(6), C33–Si2–C27 123.39(8), C33–Si2–Si1 111.85(6), C27–Si2–Si1 110.60(6).
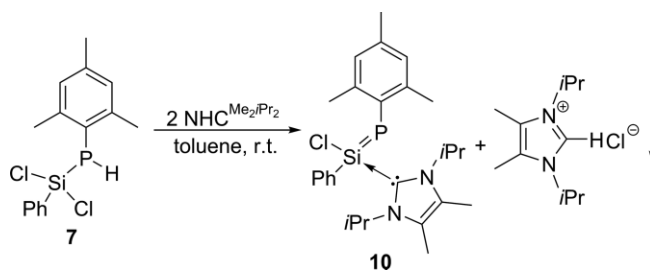
A possible mechanism for the synthesis of **8** and **9** is proposed according to the previous literature.[17a] The Si–P bond of bis(trichlorosilyl)phosphane IsP(SiCl$_3$)$_2$ easily breaks into phosphinidene active intermediates IsP and SiCl$_2$ in the presence of KC$_8$. Herein the reduction of MesP(H)SiPhCl$_2$ (**7**) by KC$_8$ resulted in the formation of short-lived Intermediates MesPH and SiPh with elimination of 6 equiv. of KCl. The intermediates MesPH and SiPh reacted rapidly. On the one hand the dimerization of SiPh with cAAC^{Me} in a ratio of 1:1 affords (cAAC^{Me}:)Si$_2$Ph$_2$
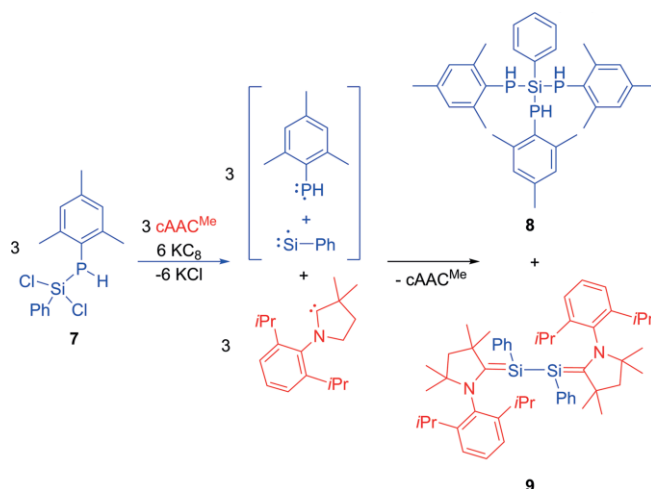
Scheme 3. The proposed mechanism for the formation of **8** and **9**.

(**9**). On the other three equiv. of MesPH attack one equiv. of SiPh to give (MesPH)$_3$SiPh (**8**), shown in Scheme 3.

When MesPH$_2$ is treated with nBuLi and PhSiCl$_3$ successively in a ratio of 3:3:1, compound **8** is obtained in a good yield. In addition, MesP(H)SiPhCl$_2$ (**7**) was treated with N-heterocyclic carbene (IiPr$_2$Me$_2$) in a molar ratio of 1:2 to afford the Lewis acid–base complex MesP=Si(Ph)Cl(IiPr$_2$Me$_2$) (**10**) in 53 % yield with a Si=P and a Si–Cl bond. (see Scheme 4) MesP(H)SiPhCl$_2$ was treated with 2 equiv. of IiPr$_2$Me$_2$. One equivalent reduces **7** by deprotonation of the P–H function and dehalogenation of the Si–Cl residue. It precipitates as IiPr$_2$Me$_2$ hydrochloride. The second carbene donates to the silicon atom in MesP=Si(Ph)Cl. Compound **10** was characterized by single-crystal X-ray diffraction (Figure 4) and NMR spectroscopy. The Si1=P1 bond length of only 2.1235(5) Å exhibits double bond character when compared with corresponding distances found in **3** [2.095(3) Å][11a] and **5** [e.g. 2.1585(9)].[9] The Si=P bond does not affect the Si=P–C angle of 103.97(4)° which is close to that in **8**. Additionally, the Si1–C1 bond length of 1.9250(13) Å is obviously longer when compared with Si1–C12 [1.8819(13) Å], emphasizing the weaker donor-acceptor abilities of the NHC compared to the cAAC. In the ^{1}H NMR spectrum of **10** three singlet resonances appear for o-C$_6$H$_2$Me$_2$ (δ = 1.38 ppm), p-C$_6$H$_2$Me (δ = 2.23 ppm), C–Me (δ = 3.12 ppm) in a ratio of 2:1:2. The ^{31}P NMR shows a resonance at δ = –144.53 (s) and the ^{29}Si NMR exhibits a resonance at δ = 0.758 (d, J = 46.4). The resonances are within a

Scheme 4. Syntheses of phosphasilene **10** from the reaction of **7** with IiPr$_2$Me$_2$.

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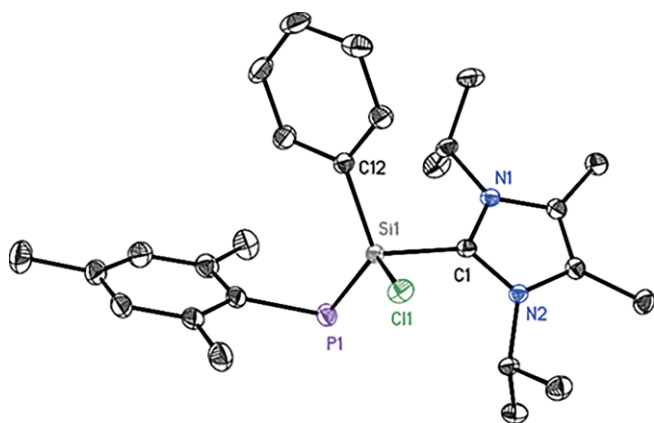European Chemical
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Figure 4. X-ray single-crystal structure of **10**. Anisotropic displacement parameters are depicted at the 50 % probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–P1 2.1235(5), Si1–Cl1 2.1712(5), Si1–C12 1.8819(13), Si1–C1 1.9250(13), P1–Si1–C12 123.24(4), P1–Si1–C1 102.75(4), P1–Si1–Cl1 122.81(2), C1–Si1–C12 108.85(5), C1–Si1–Cl1 98.78(4), Cl1–Si1–C12 97.59(4).

reasonable range, slightly different from **5** (^{31}P NMR, $\delta = -186.8$ to -216.8; ^{29}Si NMR, $\delta = -32.9$ to -26.7).[9]

IDipp [1,3-bis(2,6-iPr$_2$C$_6$H$_3$)imidazol-2-ylidene] was also explored to reduce MesP(H)SiPhCl$_2$ (**7**). We failed to get any crystals or clean product possibly due to the less stable resulting products or larger steric hindrance compared with IiPr$_2$Me$_2$/cAAC^{Me}. A comparable example was previously reported.[9] Compound **10** is well defined in comparison to **5** from Figure 2. The sterically bulky group Ter (Ter = 2,6-Tip$_2$C$_6$H$_3$, Tip = 2,4,6-iPr$_3$C$_6$H$_2$) in the latter is replaced with the much smaller Ph group in **10**. Noteworthy, we succeeded in the preparation of a Si–Cl function in a phosphasilene. This modification will increase its reactivity and application, because it can readily be replaced by any other substituent.

Conclusion

In summary, we have discovered a new synthetic route for the formation of (MesPH)$_3$SiPh (**8**) accompanied with the very interesting (cAAC^{Me}:)Si$_2$Ph$_2$ (**9**) as a by-product from the reduction of MesP(H)SiPhCl$_2$ with cAAC in the presence of KC$_8$. Furthermore, treatment of MesP(H)SiPhCl$_2$ with IiPr$_2$Me$_2$ resulted in a well-defined phosphasilene (**10**) stabilized by IiPr$_2$Me$_2$ with Si=P and Si–Cl functions, appreciated in any ligand design.

Experimental Section

General Procedures

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk 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 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$_6$D$_6$ and [D$_8$]THF were dried by stirring for 2 days over Na/K alloy followed by distillation in vacuo and degassing. 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. MesPH$_2$[9,26] and cAAC^{Me}[19] were synthesized according to the previous literature procedures.

Synthesis of MesP(H)Si(Ph)Cl$_2$ (7): nBuLi (2.5 M in hexanes) (4.0 mL, 10 mmol) was added dropwise to a diethyl ether solution (30 mL) of MesPH$_2$ (1.521 g, 10 mmol) at –78 °C. Then the reaction was warmed up to room temperature and stirred for another 4 h. PhSiCl$_3$ (2.10 g, 1.6 mL, 10 mmol) was slowly added to the resulting lithium mesityl phosphanide (MesPHLi) at –78 °C. Then the reaction was warmed up to room temperature and stirred overnight. Subsequently all volatiles were removed under vacuum, and the residue was extracted with n-hexane (50 mL), giving compound **7** as a colorless liquid after removing n-hexane under vacuum. **7** was not completely clean but contaminated with a small amount of MesPH$_2$ and PhSiCl$_3$ identified in the ^{1}H NMR, ^{31}P NMR, and ^{29}Si NMR spectra. Peak integration proves a purity of about 70 %. ^{1}H NMR (300 MHz, THF): $\delta = 7.64$–7.39 (m, 5 H, ArH), 6.89 (s, 2 H, MesH), 3.96 (d, $J = 35.4$, 1 H, PH), 2.29 (s, 6 H, –CH$_3$), 2.25 (s, 3 H, –CH$_3$). ^{13}C NMR (75 MHz, THF): $\delta = 142.25$ (s), 142.10 (s), 138.05 (s), 133.11 (s), 131.75 (s), 129.13 (d, $J = 3.75$ Hz), 128.69 (s), 128.23 (s), 22.99 (d, $J = 11.5$ Hz), 20.11 (s). ^{31}P{H} NMR (121 MHz, THF): $\delta = -145.60$ (s). ^{29}Si NMR (99 MHz, THF): $\delta = 18.583$ (d, $J = 56.5$ Hz). MS (ESI): m/z: 326.0214, found 327.0 [The detailed NMR data were obtained by comparing the crude MesP(H)Si(Ph)Cl$_2$ with MesPH$_2$, see Supporting Material].

Synthesis of (cAAC^{Me}:)Si$_2$Ph$_2$ (8) and (MesPH)$_3$SiPh (9): cAAC^{Me}·LiOTf (442 mg; 1.0 mmol) and KC$_8$ (270 mg, 2.0 mmol) were placed in a 100 mL round-bottom Schlenk flask and 20 mL of THF was added. The solution of MesP(H)Si(Ph)Cl$_2$ (purity:70 %) (0.465 g, 1.0 mmol) in THF (10 mL) was added to this mixture at –78 °C, and the reaction was warmed up to room temperature and stirred overnight giving an orange-red solution. Then the volatiles were 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. Colorless crystals of **8**, small yellow crystals of **9** together with some white solid were obtained from n-hexane after three weeks. We failed to separate crystals of **9** from the white solid (including an excess of cAAC^{Me} according to the ^{1}H NMR of the mixture) to get sufficient pure product of **9**. Crystalline (MesPH)$_3$SiPh (**8**) was characterized by NMR spectroscopy together with some MesPH$_2$. Furthermore, crystals of **8** were also obtained via the reaction of MesPH$_2$ with nBuLi and PhSiCl$_3$ successively in a ratio of 3:3:1, also some MesPH$_2$ accompanied the crystals according to ^{1}H NMR and ^{31}P NMR spectra. Total yield (including MesPH$_2$): 0.174 g (purity: 45 % determined by ^{1}H NMR); yield: 66 %. Mp: 97.3–106.4 °C. ^{1}H NMR (300 MHz, THF): $\delta = 7.29$–7.04 (m, 5H, ArH), 6.79 (s, 6H, MesH), 2.23 (s, 6H, Mes–CH$_3$), 2.22 (s, 3H, Mes–CH$_3$), 2.17 (s, 12H, Mes–CH$_3$), 2.12 (s, 6H, Mes–CH$_3$). ^{13}C NMR (75 MHz, THF): $\delta = 141.77$ (s), 140.50 (d, $J = 10.6$ Hz), 136.82 (d, $J = 4.8$ Hz), 134.30 (s), 129.08 (s), 128.69 (d, $J = 4.0$ Hz), 128.25 (d, $J = 2.4$ Hz), 127.28 (s), 22.34 (s), 22.21 (s), 20.02 (s). ^{31}P{H} NMR (121 MHz, THF): $\delta = -158.30$ (s). MS (ESI): m/z: (MesPH)$_3$SiPh (**8**), 558.69, found 559.2, MesPH$_2$, 168.21, found 169.1. (The detailed NMR data was determined via the comparison of crude **8** with MesPH$_2$ and **7**, see supporting information).

Synthesis of MesP=Si(Ph)Cl(IiPr$_2$Me$_2$) (10): IiPr$_2$Me$_2$ (360 mg; 2.0 mmol) and MesP(H)Si(Ph)Cl$_2$ (purity:71 %) (0.450 g, 1.0 mmol) were placed in a 100 mL round-bottom Schlenk flask and 40 mL of toluene was added at room temperature. The reaction was stirred overnight resulting in a red-orange solution and precipitate. After

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filtration, the concentrated filtrate was stored at room temperature and yellow crystals of **10** were obtained from solution after two days. Total yield: 0.249 g (53 %). Mp: 186.7–190.6 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.00 (s, 2H, MesH), 5.67 (dtd, J = 13.8, 7.0, 2.4 Hz, 2H, –CH), 3.12 (s, 6H, C–CH_3), 2.23 (s, 3H, Mes–CH_3), 1.38 (s, 6H, Mes–CH_3), 1.07 (d, J = 7.0 Hz, 6H, –$CH(CH_3)_2$), 0.90 (d, J = 7.0 Hz, 6H, –$CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6): δ = 144.02 (d, J = 8.9 Hz), 140.13 (s), 135.99 (s), 132.42 (s), 130.90 (d, J = 3.8 Hz), 129.59 (d, J = 4.3 Hz), 128.49 (s), 128.42 (s), 127.11 (s), 52.20 (d, J = 7.0 Hz), 27.30 (d, J = 11.4 Hz), 24.69 (s), 21.08 (d, J = 2.52 Hz), 20.68 (s), 9.92 (s). ^{31}P NMR (121 MHz, THF): δ = −144.53 (s). ^{29}Si NMR (99 MHz, C_6D_6): δ = 0.758 (d, J = 46.4). Elemental analysis found in % (calcd) for $C_{26}H_{36}ClN_2PSi$ (470.21): C, 66.29; H, 7.70; N, 5.95. Found C, 66.50; H, 7.64; N, 5.78.

Crystallographic Investigations

Crystals of **8**, **9**, **10** suitable for X-ray measurement, were grown from *n*-hexane at low temperatures. Crystal data for **8** at 100(2) K: $C_{33}H_{41}P_3Si$, M_r = 558.66 g/mol, 0.40 × 0.30 × 0.20 mm, orthorhombic, P_{bca}, a = 13.877(2) Å, b = 15.210(2) Å, c = 29.568(3) Å, V = 6240.9(14) Å^3, Z = 8, μ (Mo-K_α) = 0.249 mm^{-1}, θ_{max} = 26.4°, 49347 reflections measured, 6392 independent (R_{int} = 0.0514), R_1 = 0.0397 [$I > 2\sigma(I)$], wR_2 = 0.0991 (all data), res. density peaks: 0.439/−0.199 eA^{-3}, CCDC: 1991453. Crystal data for **9** at 100(2) K: $C_{52}H_{72}N_2Si_2$, M_r = 781.29 g/mol, 0.43 × 0.33 × 0.18 mm, monoclinic, $P2_1/n$, a = 14.681(2) Å, b = 17.680(2) Å, c = 18.843(3) Å, β= 107.92(2)° V = 4653.6(12) Å^3, Z = 4, μ (Mo-K_α) = 0.112 mm^{-1}, θ_{max} = 26.4°, 77189 reflections measured, 9570 independent (R_{int} = 0.0527), R_1 = 0.0523 [$I > 2\sigma(I)$], wR_2 = 0.1392 (all data), res. density peaks: 1.051/−0.252 eA^{-3}, CCDC: 1991454. Crystal data for **10** at 100(2) K: $C_{26}H_{36}ClN_2PSi$, M_r = 471.08 g/mol, 0.39 × 0.18 × 0.16 mm, monoclinic, $P2_1/n$, a = 9.057(2) Å, b = 17.726(3) Å, c = 16.523(2) Å, β = 94.09(2)°, V = 2645.9(8) Å^3, Z = 4, μ (Mo-K_α) = 0.266 mm^{-1}, θ_{max} = 26.4°, 77057 reflections measured, 5450 independent (R_{int} = 0.0284), R_1 = 0.0279 [$I > 2\sigma(I)$], wR_2 = 0.0732 (all data), res. density peaks: 0.370/−0.174 eA^{-3}, CCDC: 1991455 The data were integrated with SAINT.[27] A multi-scan absorption correction was applied using SADABS.[28] The structures were solved by SHELXT[29] and refined on F^2 using SHELXL[30] in the graphical user interface ShelXle.[31]

Deposition Number(s) 1991453 (for **8**), 1991454 (for **9**), and 1991455 (for **10**) contain(s) 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.ac.uk/structures.

Acknowledgments

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