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Extremely bulky secondary phosphinoamines as substituents for sterically hindered aminosilanes†

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The synthesis of a series of extremely bulky secondary amines with a phosphine function, $Ar^{\dagger}(PR_2)NH$ ($Ar^{\dagger}$ = $C_6H_2\{C(H)Ph_2\}_2Pr^i$-2,6,4; R = Ph, NEt_2, NPr^i_2) is described. Deprotonation with either *n*-BuLi or KH yields the respective alkali metal amides in some cases. Their reaction with the chlorosilanes $SiCl_4$, $HSiCl_3$, Cl_2SiPh_2, $Cl_3Si–SiCl_3$ and Si_5Cl_{10} allows access to monomeric molecular compounds bearing the extremely bulky amino substituents *via* salt elimination. The products obtained may serve as precursors for subsequent reduction reactions to access sterically protected low valent and low coordinate silicon compounds.

Introduction

During the past three decades of main group chemistry, many compounds with hitherto unknown bonding motifs and oxidation states have been discovered.[1] Especially, low-coordinate/low-oxidation state main group complexes have attracted not only the attention of preparative chemists but also of theoreticians. The utilization of sterically demanding ligand systems has allowed the stabilization of compounds which were previously thought to be too reactive to be isolated on a preparative scale. The further chemistry of these reactive complexes has also rapidly emerged in recent years. This is perhaps best exemplified by the 2005 report by Power *et al.*, which described the facile activation of hydrogen by a digermyne, a reaction motif that is typical for late d-block metal complexes.[2] Further research revealed similar reactions for other low oxidation state main group compounds, including the activation of H_2, NH_3, CO and CO_2.[3] Many results in this field were achieved by using polydentate ligand systems (*e.g.* β-diketiminates), or additional Lewis-bases, to stabilize these highly reactive compounds.[4,5] However, within the research of low-oxidation state group 14 element compounds, remarkable results have been reported for unsupported and thus low-valent species.[6,7] Most recently, the synthesis of unsupported two-coordinate amido germanium(II) and tin(II) hydrides using the extremely bulky amido ligand $(Ar^{\dagger})(SiPr^i_3)N–(Ar^{\dagger} = C_6H_2\{C(H)Ph_2\}_2Pr^i$-2,6,4) allowed their application as highly efficient catalysts for hydroboration reactions.[7,8] A specific focus of the research presented here is on related silicon compounds as they perfectly meet the criteria for non-toxic, abundant and inexpensive replacements for transition metal complexes for use in chemical transformations, be they stoichiometric or catalytic. However, access to low-coordinate silicon(II) species is a challenging endeavor and no example of a two-coordinate chloro or hydrido silylene has yet been reported. Herein, new extremely bulky secondary amides with a phosphine function, and their application as ligands for the synthesis of aminosilane compounds, are presented. The latter hold significant potential as precursors for two-coordinate low-oxidation state silicon systems.

Results and discussion

Recently, our group reported a series of secondary amines, substituted with aryl and silyl groups of varying steric bulk of the type $(Ar)(SiR_3)NH$ (Ar = $Ar^{\dagger}$ or Ar* = $C_6H_2\{C(H)Ph_2\}_2$Me-2,6,4; R_3 = Me_3, Ph_3, Pr^i_3, Ph_2Me), in addition to their utilization as pro-ligands for the stabilisation of two-coordinate amido-group 14 halide complexes.[9,10] The commercial availability of stable germanium(II), tin(II) and lead(II) chlorides (ECl_2, E = Ge, Sn or Pb) allowed for the straightforward substitution of one chloride ligand on these precursors with a bulky amino substituent *via* salt methathesis reactions using alkali metal amide reactants. In contrast with the heavier homologues, there is no commercial source of silicon(II) halides, and instead low oxidation state silicon compounds are typically accessed *via* reduction of silicon(IV) precursor complexes derived from $SiCl_4$ and $HSiCl_3$.[4,11,12] With that said, the previously synthesized bulky aminosilanes $(Ar*)(SiR_3)N–SiCl_3$ and $(Ar*)(SiMe_3)N–SiCl_2H$ could not be reduced to lower oxidation silicon compounds. To overcome these limitations, we proposed to replace the silyl group of the ligand with a bulky phosphine group. The resultant phosphinoamide system was

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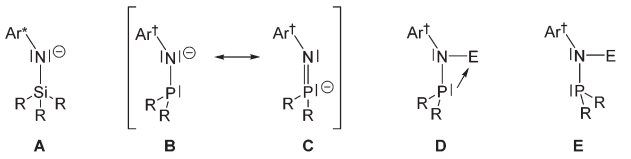
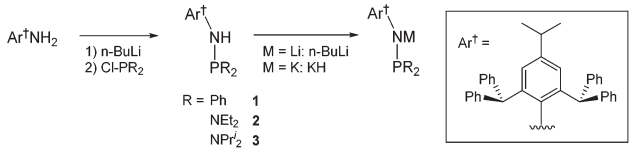


Fig. 1 Comparison between silylamido (A) and phosphinamido ligands (B and C) coordinated to a tetrel fragment E. The P-lone pair of the latter can coordinate E (D) or not (E), depending on steric and electronic factors.



Scheme 1 Synthesis of the pro-ligands **1–3** and their respective alkali metal amides.

seen as offering both a different steric and electronic environment, as well as an additional, and potentially donating, lone pair at the phosphorus adjacent to the nitrogen atom. In this respect, it is well known that phosphinoamides have a significantly shortened P–N bond with the negative charge mainly located at the nucleophilic nitrogen-atom (B, Fig. 1). Accordingly, this class of ligand has a long history in the coordination chemistry of transition and alkali metals.[13] However, there are only few reports of bulky phosphinoamides being utilised for the kinetic stabilization of low valent main group compounds.[14,15] The synthesis of phosphinoamides with even greater steric bulk was an initial target of this study.

In order to access extremely bulky phosphinoamides, the three amine pro-ligands $Ar^{\dagger}(PR_2)NH$ (R = Ph, NEt_2, NPr^{i}_2) were synthesized using modifications of literature procedures (Scheme 1).[16,17]

Compared with previously reported, and less sterically demanding analogues, the extreme steric bulk of the $Ar^{\dagger}$ group did not negatively affect the yield of the products significantly. The molecular structures of the phosphinoamines each show the expected planar nitrogen and pyramidal phosphorus geometry (Fig. 2). Selected structural parameters are given in Table 1.

Compounds **1** and **2** were readily deprotonated using *n*-BuLi or KH/HDMS, as monitored by ^{31}P NMR spectroscopy, and were used *in situ* for further reactions with no isolation or purification necessary. The phosphinoamine **3** not only pro-

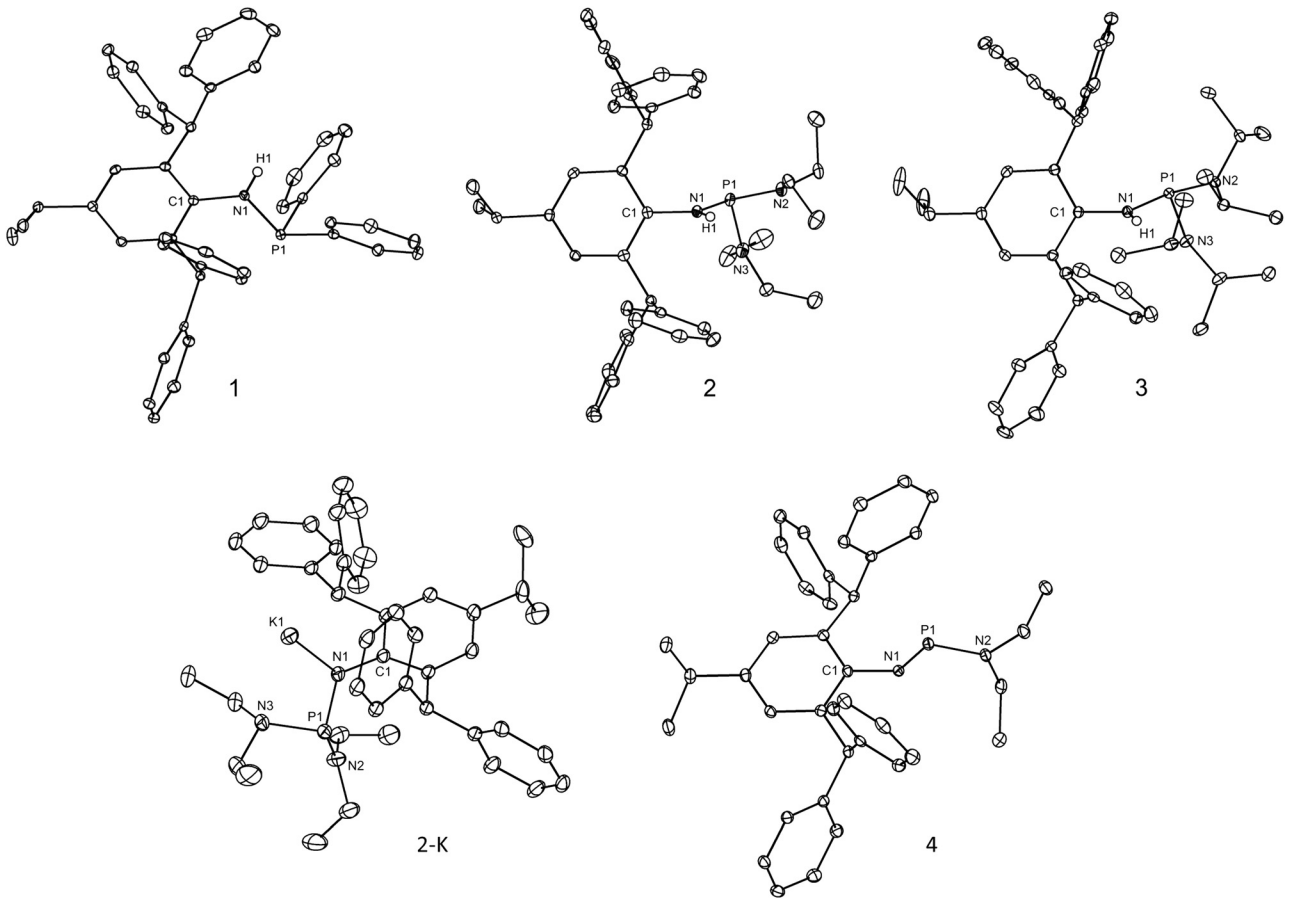


Fig. 2 Molecular structures of the amine pro-ligands **1**, **2**, **3**. **2-K** and **4** with the thermal ellipsoid plots at the 25% probability level. Hydrogen atoms, except the N–H atoms, are omitted for clarity. Selected structural parameters are given in Table 1.

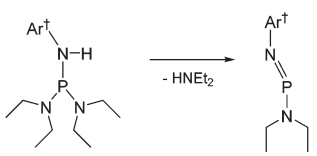
Table 1 Selected bond lengths (Å) and angles (°) for compounds **1–3**, **2-K** and **4** and $^{31}P\{^1H\}$ NMR chemical shifts (δ)

	1	**2**	**3**	**2-K**	**4**
N1–C1	1.428(2)	1.437(3)	1.421(2)	1.383(3)	1.405(3)
N1–P1	1.711(2)	1.709(2)	1.723(1)	1.649(3)	1.561(2)
N2–P1	—	1.709(2)	1.696(1)	1.704(3)	1.645(2)
N3–P1	—	1.691(2)	1.695(1)	1.751(3)	—
N1–K	—	—	—	2.654(3)	—
N3–K	—	—	—	2.954(3)	—
C1–N1–P1	121.1(1)	119.0(2)	120.3(1)	125.9(2)	124.8(2)
Ang. sum (P)	303.6(1)	307.0(1)	312.1(1)	310.0(2)	—
^{31}P NMR	38.2	102.5	78.0	91.9	270.2

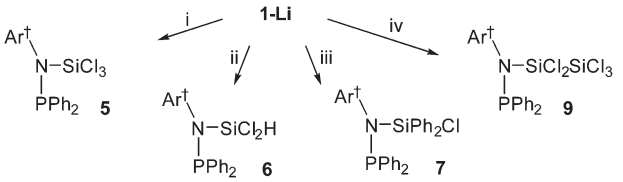
vides the extreme steric bulk of the Ar†-substituent, but additional bulk comes from the $-P(NPr^i_2)_2$ group. Unfortunately, it was not possible to deprotonate **3**, following the same synthetic protocols as used for **1** and **2**. This result can be attributed to the high demand of steric bulk around the amine proton, rather than to electronic factors, as **2** and **3** share very similar electronic environments at the amine nitrogen atom. In an attempt to prepare a chloro-aminosilane(III), the potassium salt of **2** (**2-K**) was slowly added to a solution of $Cl_3Si–SiCl_3$ in toluene at −78 °C. A significant downfield shift in the ^{31}P NMR spectrum from δ 91.9 (**2-K**) to δ 270.2 ppm (product) was observed. A single crystal XRD study of the product revealed that it is not a silicon containing product, but rather the phosphinoimine **4** (Fig. 2), presumably formed by an elimination reaction. Similar elimination reactions have been reported previously,[18] although in this case the formation of **4** proceeds spontaneously at low temperatures and the product is essentially stable as a solid. The mechanism of this reaction is not fully understood, however, it was observed that the free phosphinoamine **2** undergoes slow decomposition in solution, in the absence of other reactants, to yield **4** *via* elimination of $HNEt_2$, as monitored by ^{31}P NMR spectroscopy (Scheme 2). It should be noted that related reactions of the lithium or potassium salts of **2** with $SiCl_4$ led to intractable product mixtures.

As the phosphinoamines **2** and **3**, and alkali metal salts of **2**, were found to be not suitable for the synthesis of sterically protected aminosilanes, lithiated **1** was explored as a precursor for salt metathesis reactions with chlorosilanes. In this respect, addition of **1-Li** to $SiCl_4$, $HSiCl_3$ and Ph_2SiCl_2 readily yielded compounds **5**, **6** and **7**, respectively (Scheme 3).

While amido analogues of compounds of **5**, **6**, and phosphinoamido analogues of **5** have been reported earlier,[15] the compound type represented by **7**, appears without precedent.[9] The crystal structures of **5** and **7** revealed a different role of the



Scheme 2 Decomposition of **2** to yield **4**.



Scheme 3 Synthesis of compounds **5**, **6**, **7** and **9** by addition of **1-Li** to a solution of the respective chlorosilane *via* elimination of LiCl. (i) $SiCl_4$; (ii) $HSiCl_3$; (iii) Ph_2SiCl_2; (iv) $Cl_3Si–SiCl_3$.

lone pair at the phosphorus atom in each (Fig. 3). The P-lone pair in compounds **5** and **6** is pointing away from the silicon center, whereas in compound **7** the lone pair is directed towards it, but without P–Si coordination taking place. This difference may be attributed to steric repulsion between the phenyl groups at the phosphorus and at the $SiPh_2Cl$ fragment in compound **7**. It is of note that the change of the amide ligand from that in Ar*(SiMe$_3$)N–SiCl$_3$ to that in Ar†(PPh$_2$)N–SiCl$_3$ caused only minor structural changes. For example, the N–Si (1.693(8) Å) and the mean Si–Cl (2.026(4) Å) bond lengths in **5** are slightly longer compared to the respective bond lengths in Ar*(SiMe$_3$)N–SiCl$_3$ (1.74(2) and 2.010(2) Å).

Compounds **5**, **6** and **7** were found to be surprisingly stable towards several reducing agents. Attempts at reducing the aminosilanes with $\{(^{Mes}Nacnac)Mg\}_2$ ($^{Mes}Nacnac$ = $[(MesNCMe)_2CH]^-$, Mes = mesityl)[19] or KC_8 in toluene showed no reaction, as determined by ^{31}P NMR spectroscopy. When elemental potassium or KC_8 in thf were used, complete decomposition of the starting materials was observed. The addition of the N-heterocyclic carbene (NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) as a dehydrochlorinating reagent to a solution of **6** in toluene afforded the free phosphinoamine, **1**, as the only phosphorus-containing compound. Attempts to reduce **5** and **6** with potassium naphthalide led to no reaction. On the other hand, addition of one equivalent of potassium naphthalide to a solution of **7** showed consumption of *ca.* 50% of the starting material and the formation of a new product (^{31}P NMR: δ −28.3 ppm).

Interestingly, crystallization of the reaction mixture yielded only one phosphorus free product, that is the potassium amide K[Ar†(SiPh$_2$Cl)N], presumably formed *via* a P–N cleavage reaction. Unfortunately, the XRD data for the crystal structure of the potassium amide were not of publishable quality, but the structure did confirm the gross atomic connectivity in the salt. When the reaction was repeated using two equivalents of potassium naphthalide, complete consumption of the starting material was observed, according to Scheme 4. This allowed assignment of the signal at δ −28.3 ppm in the ^{31}P NMR spectrum of the reaction mixture, to the potassium phosphide, K[PPh$_2$], which arises from potassium induced P–N bond cleavage in **7**.[20] It is noteworthy that in the ESI mass spectrum of **7**, a signal at m/z = 683.5 a.u. was detected and assigned to $[H_2N(Ar^†)(SiPh_2Cl)]^+$, further supporting the facility of P–N cleavage reactions for the aminosilane. Similar P–N cleavage reactions provide a plausible explanation for the decompo-

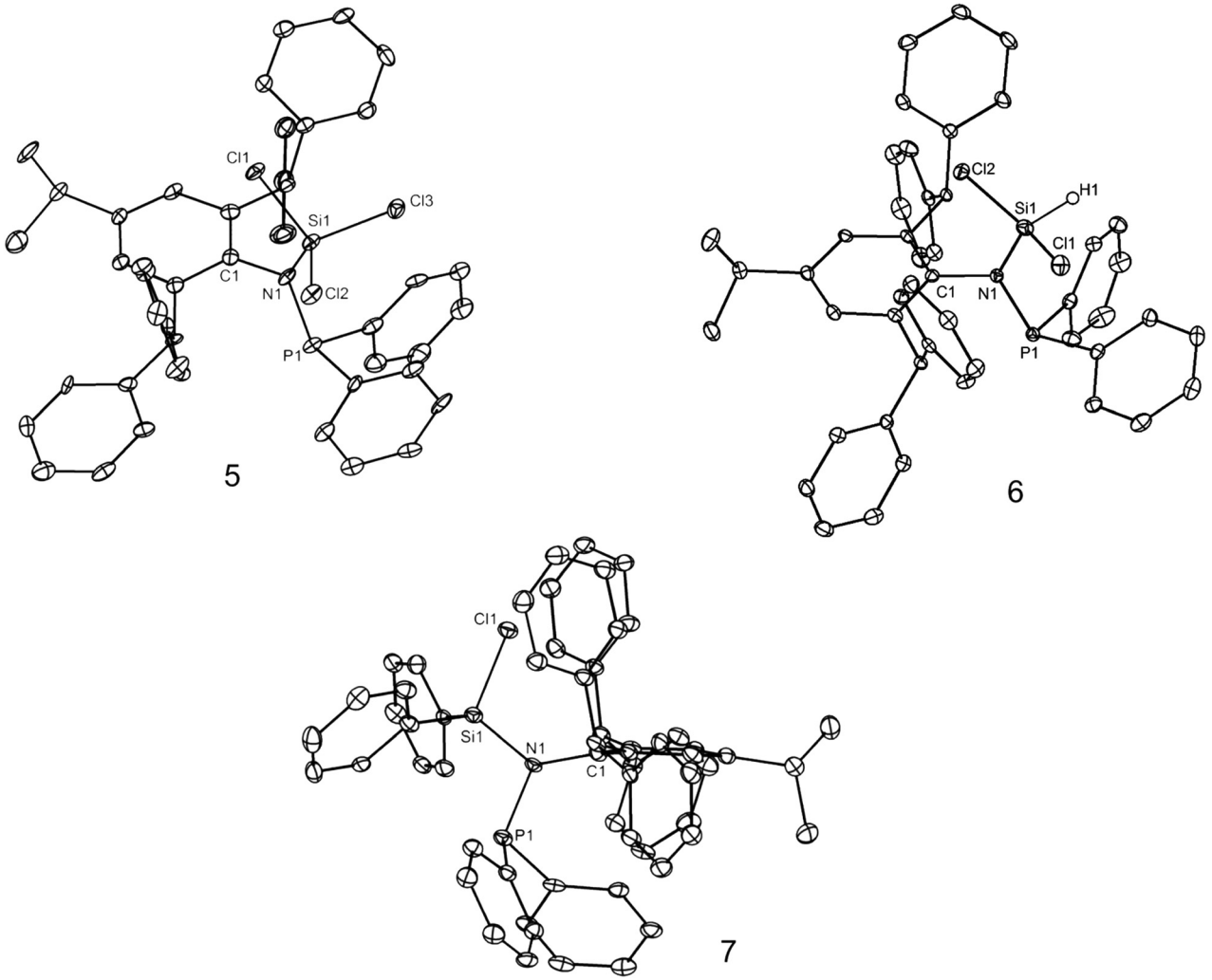
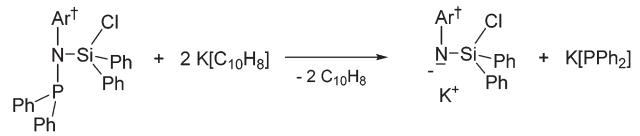


Fig. 3 Molecular structures of **5**, **6** and **7** with the thermal ellipsoid plots at the 25% probability level. Hydrogen atoms, except the Si–H atom of **6**, are omitted for clarity. Selected bond lengths (Å) and angles (°) for **6**: N1–C1 1.466(5), N1–P1 1.760(3), N1–Si1 1.707(4), Si1–Cl1 2.025(2), Si1–Cl2 1.980(2), C1–N1–P1 111.8(2), C1–N1–Si1 111.8(2), P1–N1–Si1 129.0(2), Σ angles at P 312.0(2). For **7**: N1–C1 1.449(6), N1–P1 1.746(4), N1–Si1 1.753(4), Si1–Cl1 2.049(2), C1–N1–P1 123.0(3), C1–N1–Si1 129.3(3), P1–N1–Si1 106.4(2), Σ angles at P 319.2(3). N.B. Structural parameters for **5** can be found in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **5**, **8**, **9** and **10** and $^{31}P\{^{1}H\}$ NMR shifts (δ)

	5	**8**	**9**	**10**
N1–C1	1.456(11)	1.440(2)	1.468(4)	1.457(2)
N1–P1	1.785(7)	1.780(6)	1.758(3)	1.731(2)
N1–Si1	1.693(8)	1.713(2)	1.717(3)	1.751(2)
Si1–Si2	—	—	2.345(2)	2.3377(9)
Mean Si1–Cl	2.026(4)	—	2.039(1)	—
Mean Si2–Cl	—	—	2.042(2)	—
P1–N1–Si1	129.9(4)	126.6(2)	106.9(2)	130.19(9)
Ang. sum (P)	313.3(4)	308.6(4)	317.9(2)	310.1(1)
^{31}P NMR	65.7	59.6	49.2	63.5

sition reactions observed in the attempted reductions of **5** and **6**. However, alkali metal amides derived from these reductions were never isolated.

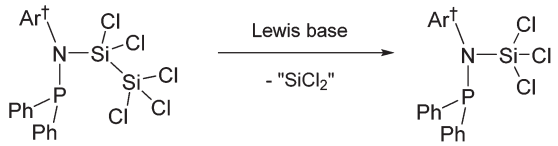


Scheme 4 Observed P–N cleavage in the reaction of **7** with $K[C_{10}H_8]$.

In an attempt to access a phosphinoamino–silicon(III) compound, addition of **1-Li** to Cl_3Si–$SiCl_3$ in toluene was carried out, which afforded compound **9** in moderate yield after work-up (Scheme 3). Compound **9** is stable as a solid under inert atmosphere for at least several weeks. In ether solutions it readily decomposes to yield **5** as the only product containing a phosphorus atom. This formal elimination of $SiCl_2$ is analogous to that previously observed for the iron(II) complex

$[Cp(CO)_2Fe–SiCl_2–SiCl_3]$, which yielded $[Cp(CO)_2Fe–SiCl_3]$ under UV-irradiation.[21]

For compound **9**, the elimination process is apparently triggered by Lewis bases (Scheme 5). In non-coordinating solvents (*e.g.* C_6D_6, toluene) the process is almost negligible. If the synthesis of **9** was carried out in diethyl ether instead of toluene, the yield decreased significantly and in thf only compound **5** was detected. When the free N-heterocyclic carbene IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was added to a solution of **9** in C_6D_6 in an attempt to trap the $SiCl_2$ fragment under formation of IPr–$SiCl_2$,[11] the reaction solution immediately showed only the resonance for **5** in its ^{31}P NMR spectrum. Unfortunately, IPr–$SiCl_2$ could not be determined as being present in the reaction mixture, based on the ^{1}H and ^{29}Si NMR spectroscopic data of that mixture. Attempts at reducing **9** with $\{^{Mes}NacnacMg\}_2$ or KC_8, again only afforded compound **5**.



Scheme 5 Lewis base induced formal elimination of $SiCl_2$ from **9** to give **5**.

So as to demonstrate the utility of the chlorosilanes **5** and **9** as precursors to the corresponding silicon hydride compounds, they were treated with an excess of $LiAlH_4$ in diethyl ether which readily yielded the silanes $(PPh_2)(Ar^{\dagger})N–SiH_3$ **8** and $(PPh_2)(Ar^{\dagger})N–SiH_2SiH_3$ **10** *via* Cl/H exchange processes. Related Cl/H exchange reactions have been reported for similar chlorosilanes.[21,22] The molecular structures of compounds **8**, **9** and **10** were determined (Fig. 4), which in the case

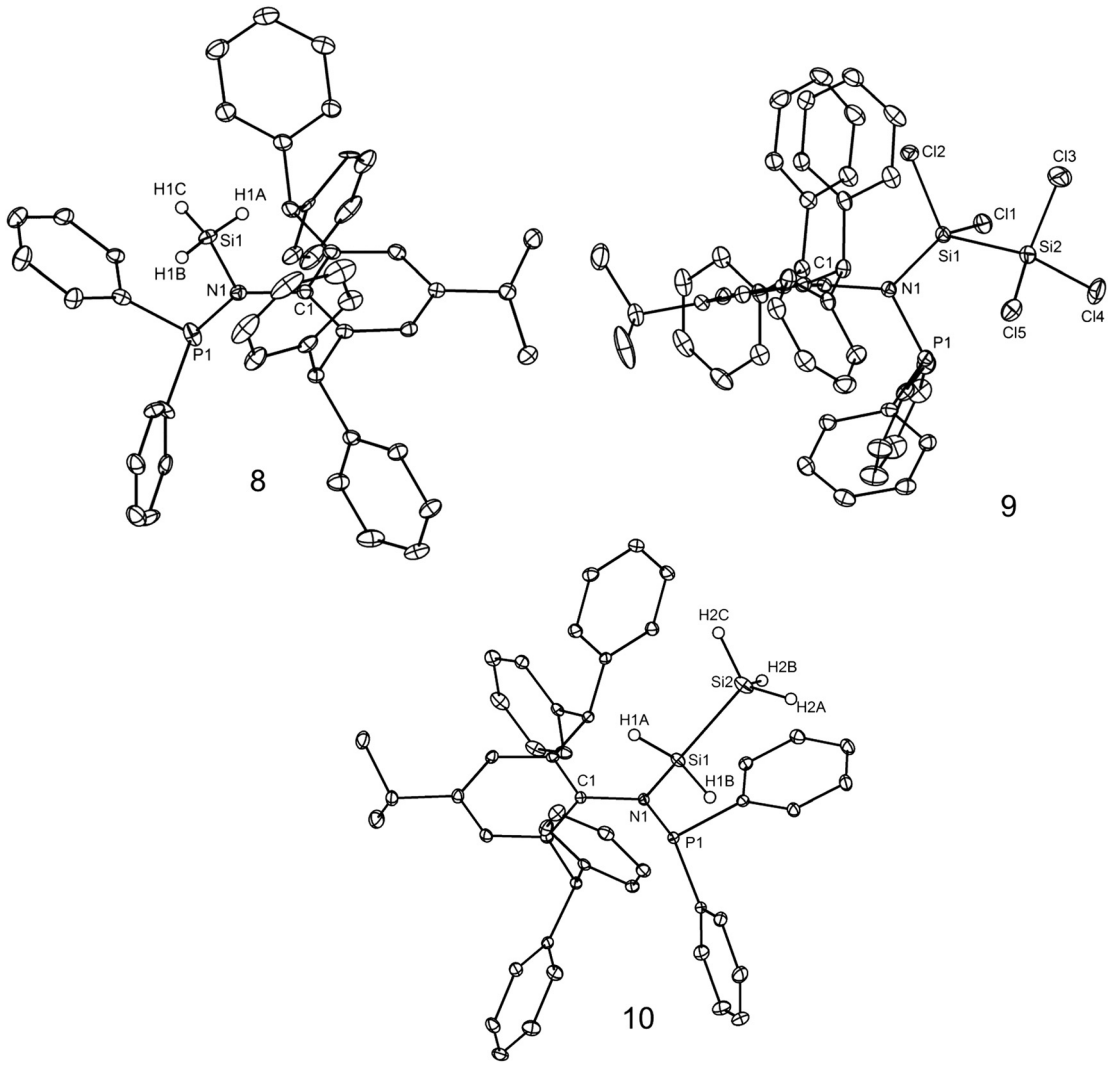
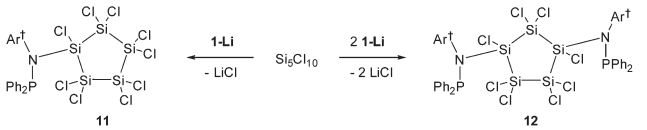


Fig. 4 Molecular structures of **8**, **9** and **10** with the thermal ellipsoid plots at the 25% probability level. Hydrogen atoms, except the Si–H atoms, are omitted for clarity. Selected structural parameters are given in Table 2.

of **5** and **8**, showed the conversion of the –$SiCl_3$ moiety to the an –SiH_3 unit only slightly affects the molecular geometry of the compounds. The lone pair at the phosphorus atom is pointing away from the silicon atom in both compounds, showing no P···Si intramolecular interaction. The N1–P1 and N1–Si1 bond lengths increase on going from **5** to **8**. The P1–N1–Si1 angle is greater in **8**, which can be attributed to its less bulky –SiH_3 group compared with –$SiCl_3$ in **5**. The ^{31}P NMR spectroscopic signal for **8** (δ 59.6 ppm) is shifted slightly upfield compared with that for **5** (δ 65.7 ppm), which is in accord with the positions of the ^{29}Si NMR spectroscopic signals for **5** (δ −29.4 ppm) and **8** (δ −47.1 ppm, $^1J_{SiH}$ = 218 Hz). Moreover, the N–Si bond length in **8** (1.713(2) Å) compares well with that found for the known silylhydrazine $H_3SiMeNNMe_2$ (1.693(1) Å).[23] The two higher silanes **9** and **10** show a different involvement of their phosphorus lone pairs. In **9** the two phenyl groups at the phosphorus are turned towards the bulky Ar† group, allowing a weak interaction between P1 and Si2. That is, the P(donor)···Si(acceptor) distance is 3.555(1) Å, which is shorter than the sum of the van der Waals radii (r_{vdw}(Si–P) 3.90 Å),[24] but significantly longer than the sum of the covalent radii (2.08 Å).[25] The N1–Si1 bond length in **9** (1.717(3) Å) is shorter compared with **10** (1.751(2) Å), whereas the Si1–Si2 bond length is slightly longer in **9** (2.345(2) Å) than the one found for **10** (2.3377(9) Å). Both Si–Si bond lengths compare well with that for Ter–$SiCl_2$–$SiCl_3$ (2.358(2) Å) (Ter = 2,6-$Mes_2C_6H_3$).[26] The ^{31}P NMR spectroscopic signals for **9** (δ 49.2 ppm) and **10** (δ 63.5 ppm) are at similar chemical shifts to those for the related aminosilanes described in the Introduction. The ^{29}Si NMR spectroscopic signal for Si1 in **9** (δ −29.4 ppm) is shifted significantly upfield compared with that for Ter–$SiCl_2$–$SiCl_3$ (δ −4.24 ppm), whereas the signal for Si2 in **9** (δ −2.1 ppm) is comparable with the one found for Ter–$SiCl_2$–$SiCl_3$ (δ −3.54 ppm). For compound **10** the resonances for Si1 (δ −38.6 ppm, $^1J_{SiH}$ = 208 Hz) and for Si2 (δ −99.8 ppm, $^1J_{SiH}$ = 196 Hz) compare well with the ones detected for the iron complex [$Cp(CO)_2Fe$–SiH_2–SiH_3] (–SiH_2–: δ −45.2 ppm, $^1J_{SiH}$ = 172 Hz and –SiH_3–: δ −95.6 ppm, $^1J_{SiH}$ = 184 Hz).[21]



Scheme 6 Synthesis of compounds **11** and **12**.

To explore the chemistry of more silicon rich chloro-aminosilanes, addition of one equivalent **1-Li** to a solution of the cyclic chlorosilane Si_5Cl_{10} in toluene was carried out, and this afforded **11**. When two equivalents of **1-Li** were added to Si_5Cl_{10}, compound **12** was obtained (Scheme 6). Both compounds were isolated in moderate yields and were fully characterized.

If kept under an inert atmosphere, both **11** and **12** are stable, however, in solution compound **10** slowly decomposes and signals for **5** and the free amine, **1**, were detected by ^{31}P NMR spectroscopy. In contrast, compound **12** is stable in solution for at least several days and does not undergo a similar decomposition reaction. The ^{31}P NMR spectroscopic signals for **11** (δ 51.9 ppm) and **12** (δ 42.2 ppm) both appear as sing-

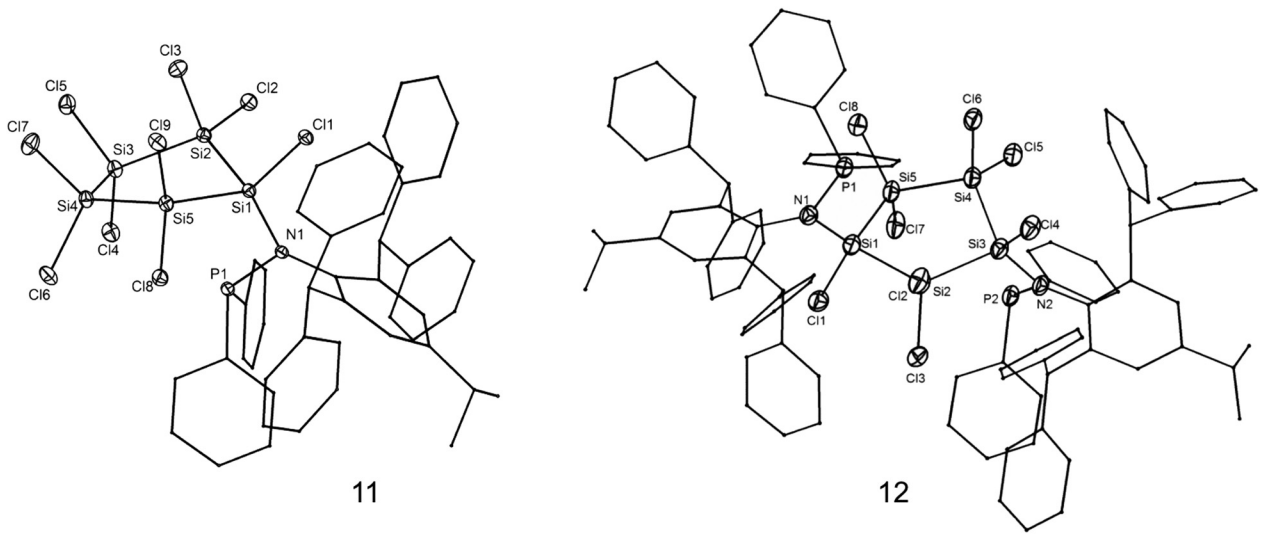


Fig. 5 Molecular structures of **11** and **12** with the thermal ellipsoid plots at the 25% probability level. Hydrogen atoms are omitted for clarity. All carbon atoms are depicted using a "wire" representation. Selected bond lengths (Å) and angles (°) for **11**: N1–C1 1.468(5), N1–P1 1.738(3), N1–Si1 1.719(3), Si1–Si2 2.366(2), Si2–Si3 2.347(2), Si3–Si4 2.351(2), Si4–Si5 2.370(2), Si1–Si5 2.398(2), Si1–Cl1 2.034(2), C1–N1–P1 123.8(2), P1–N1–Si1 101.9(2), Σ angles at P 318.7(2). And **12**: N1–C1 1.460(1), N1–P1 1.740(9), N1–Si1 1.735(9), Si1–Si2 2.390(5), Si2–Si3 2.400(5), Si3–Si4 2.357(5), Si4–Si5 2.355(4), Si5–Si1 2.356(5), Si1–Cl1 2.040(4), N2–C48 1.46(2), N2–P2 1.721(9), N2–Si3 1.731(9), Si3–Cl4 2.044(4), C1–N1–P1 126.7(7), P1–N1–Si1 101.1(5), C48–N2–P2 127.4(7), P2–N2–Si3 102.8(5), Σ angles at P1 321.1(6) Σ angles at P2 321.4(5).

lets. Both compounds possess three chemically inequivalent silicon atoms and their ^{29}Si NMR signals appear as doublets due coupling to the phosphorus atom of the ligand. The decrease of the coupling constant on going from $^{2}J_{PSi}$ to $^{4}J_{PSi}$ allowed their assignment (see Experimental section). The high degree of kinetic stabilization of the Si_5 ring in **12** not only prevents its decomposition in solution, but also makes **12** inert towards reduction using $\{^{Mes}NacnacMg\}_2$ or KC_8 in toluene (used either equimolar or in excess). Compound **11**, substituted with only one amido ligand, showed complete decomposition to as yet unidentified product mixtures following the same synthetic approaches.

To date, only mono-aryl substituted cyclic, five-membered chlorosilanes have been structurally characterized,[22] and other related five-membered cyclic silianes were obtained by different synthetic approaches.[27] The molecular structures of **11** and **12** were successfully determined by single crystal XRD (Fig. 5). The Si_5 ring in **11** adopts a distorted envelope configuration with the Si2 atom being 0.89 Å out of the least squares plane defined by Si1, Si3, Si4 and Si5. The ring in **12** shows a more puckered geometry with a less pronounced envelope-like configuration. That is, the Si4 atom is only 0.63 Å out of the least squares plane defined by Si1, Si2, Si3 and Si5. The lone pairs at the phosphorus atoms of both **11** and **12** display interatomic P···Si contacts with the silicon atom substituted by the amide ligand (in **11** 2.684(2) Å and **12** P1–Si1: 2.683(5) and P2–Si3: 2.698(4) Å), which are between the sum of the van der Waals radii (r_{vdw}(Si–P) = 3.90 Å)[24] and the sum of the covalent radii (r_{cov}(Si–P) = 2.08 Å),[25] for the two elements. The mean Si–Si bond lengths in the ring systems (**11**: 2.366(2) Å; **12**: 2.372(5) Å) are only slightly longer than that for Si_5Cl_{10}·2MeCN (2.35 Å).[28]

Conclusion

In summary, a series of novel, extremely bulky secondary phosphinoamines have been synthesised and compared with previously reported bulky aryl/silylamines. Deprotonation with *n*-BuLi or KH afforded examples of the respective alkali metal amides, which proved to be suitable ligands for different chlorosilane fragments. These include compounds derived from $SiCl_4$, and the higher homologues, $Cl_3Si–SiCl_3$ and cyclic Si_5Cl_{10}. Attempts at the reduction of the prepared chloroaminosilanes revealed them to display unexpected inertness. Furthermore, by using more rigorous conditions, a P–N bond cleavage reaction of one amido ligand was observed. The mono-amide substituted compounds derived from $Cl_3Si–SiCl_3$ and Si_5Cl_{10} decompose *via* an apparent Lewis-base triggered eliminition of $SiCl_2$. The bis-amide substituted Si_5 ring is kinetically protected by the high steric demand of two extremely bulky amido ligands. In addition, the amido-coordinated $–SiCl_3$ and $–SiCl_2–SiCl_3$ functions can undergo Cl/H-exchange reactions to yield the respective stable silanes with $–SiH_3$ and $–SiH_2–SiH_3$ fragments. The molecular structures of all species were determined and discussed.

Experimental Section

General methods

All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity dinitrogen. THF, hexane and toluene were distilled over molten potassium, while diethyl ether was distilled over Na/K (50 : 50) alloy. Deuterated benzene (C_6D_6) was dried and stored over sodium. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, ^{31}P{^{1}H} NMR, and ^{1}H/^{29}Si HMBC spectra were recorded on either a Bruker DPX300 or a Bruker AvanceIII 400 spectrometer and were referenced to the resonances of the solvent used (^{1}H and ^{13}C NMR), external TMS (^{29}Si NMR) and external 85% H_3PO_4 (^{31}P NMR). IR spectra were recorded for solid samples, protected from the atmosphere by Nujol films, using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. The starting materials $Ar^{\dagger}NH_2$,[29] $ClP(NEt_2)_2$, $ClP(NiPr_2)_2$,[30] and Si_5Cl_{10} [31] were prepared by procedures reported in the literature. All other compounds were obtained from commercial sources and used as received.

Preparation of $Ar^{\dagger}(PPh_2)NH$ (1). A solution of *n*-butyllithium in hexane (7.6 ml, 12.20 mmol) was slowly added to a solution of $Ar^{\dagger}NH_2$ (5.40 g, 11.6 mmol) in thf (80 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently cooled to −80 °C. Neat $ClPPh_2$ (2.80 g, 12.70 mmol) was added and the reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure, and the residue then extracted with toluene. The solvent was removed from the extract under reduced pressure and the remaining pale yellow solid was washed two times with hexane (20 ml). Drying *in vacuo* gave $Ar^{\dagger}(PPh_2)NH$ (5.50 g, 8.44 mmol) as a pale yellow solid. Yield: 73%. M.p.: 174–176 °C. ^{1}H NMR (C_6D_6, 400 MHz, 296 K), δ = 0.93 (d, 6H, $^{3}J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.46 (sept., 1H, $^{3}J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 3.65 (d, 1H, $^{2}J_{PH}$ = 8 Hz, N–H), 5.93 (d, 2H, $^{5}J_{PH}$ = 3 Hz, –CHPh$_2$), 6.92–7.34 (m, 32H, Ar–H). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 24.1 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.9 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 52.7 (CHPh$_2$), 126.6, 128.5, 128.7, 128.8, 129.2, 130.2, 132.0 (d, J_{CP} = 21 Hz), 139.6 (d, J_{CP} = 3 Hz), 140.9 (d, J_{CP} = 12 Hz), 142.7 (d, J_{CP} = 15 Hz), 144.1 (d, J_{CP} = 3 Hz), 144.3 (Ar–C). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 38.2. IR ν/cm^{-1} (ATR): 1598 (w), 1492 (m), 1446 (m), 1377 (w), 1354 (w), 1264 (w), 1090 (w), 1075 (w), 1029 (w), 883 (w), 865 (w), 845 (w), 745 (m), 726 (s), 692 (s). MS/EI m/z (%): 651.6 (M^+, 62), 466.4 ($Ar^{\dagger}NH^+$, 46), 167.0 (Ph_2CH^+, 35). Anal. calc. (%) for $C_{47}H_{42}NP$ (M_r = 651.83): C, 86.60; H, 6.49; N, 2.15; Found: C, 86.67; H, 6.53; N, 2.16.

Preparation of $Ar^{\dagger}(PPh_2)NLi$ (1-Li). The lithium salt was prepared according to a procedure reported in the literature, *i.e.* by reaction of **1** with a slight excess of *n*-butyllithium in toluene.[17] Compound **1-Li** is highly sensitive towards air and moisture and was therefore only prepared *in situ* for direct use. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 64.3.

Preparation of $Ar^{\dagger}\{P(NEt_2)_2\}NH$ (2). A solution of *n*-butyllithium in hexane (7.0 ml, 11.20 mmol) was slowly added to a solution of $Ar^{\dagger}NH_2$ (5.00 g, 10.7 mmol) in thf (80 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently cooled to −80 °C. Neat $ClP(NEt_2)_2$ (2.50 g, 11.77 mmol) was added and the reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the remaining pale yellow solid was extracted with hexane. The extract was kept at −30 °C to give pale yellow crystals of **2** (5.50 g, 8.57 mmol). Yield: 73%. M.p.: 101–103 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.84 (t, 12H, $^3J_{HH}$ = 7 Hz, –CH_2–CH_3), 0.93 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.47 (sept., 1H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.89 (m, 8H, –CH_2–CH_3), 3.67 (s, 1H, N–*H*), 6.50 (d, 2H, $^5J_{PH}$ = 7 Hz, –CHPh$_2$), 6.91–7.30 (m, 22H, Ar–*H*). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 15.4 (CH_2–CH_3), 24.4 ($Ar^{\dagger}$–CH(CH_3)$_2$), 34.1 ($Ar^{\dagger}$–CH(CH_3)$_2$), 40.7 (N–CH_2–), 53.3 (CHPh$_2$), 126.9, 128.7, 128.9, 130.6, 137.8, 140.0, 142.4 (Ar–*C*). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 102.5. IR ν/cm^{-1} (ATR): 1598 (w), 1493 (m), 1446 (m), 1373 (w), 1340 (w), 1289 (w), 1264 (w), 1188 (m), 1172 (m), 1124 (w), 1092 (w), 1007 (m), 910 (m), 897 (m), 878 (w), 866 (w), 830 (m), 785 (m), 763 (m), 730 (m), 697 (s). Anal. calc. (%) for $C_{43}H_{52}N_3P$ (M_r = 641.88): C, 80.46; H, 8.17; N, 6.55; Found: C, 80.35; H, 8.28; N, 6.49.

Preparation of $Ar^{\dagger}\{P(NEt_2)_2\}NK$ (2-K). The potassium salt was prepared according to a procedure reported in the literature, *i.e.* by reaction of **1** with KH/HMDS.[32] Compound **2-K** is highly sensitive towards air and moisture and was therefore only prepared *in situ* for direct use. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 91.9.

Preparation of $Ar^{\dagger}\{P(NiPr_2)_2\}NH$ (3). A solution of *n*-butyllithium in hexane (7.0 ml, 11.20 mmol) was slowly added to a solution of $Ar^{\dagger}NH_2$ (5.00 g, 10.7 mmol) in thf (100 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently cooled to −80 °C. A solution of $ClP(NiPr_2)_2$ (2.99 g, 11.20 mmol) in thf (30 ml) was added and the reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the remaining pale yellow solid was extracted with hexane. The extract was kept at −30 °C to give pale yellow crystals of **3** (4.50 g, 6.45 mmol). Yield: 58%. M.p.: 136 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.93 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 0.97 (d, 12H, $^3J_{HH}$ = 7 Hz, –NCH(CH_3)$_2$), 1.17 (d, 12H, $^3J_{HH}$ = 7 Hz, –NCH(CH_3)$_2$), 2.48 (sept., 1H, $^3J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 3.34 (m, 4H, $^3J_{HH}$ = 7 Hz, –NCH(CH$_3$)$_2$), 3.72 (s, 1H, N–*H*), 6.50 (m, 2H, –CHPh$_2$), 6.89–7.33 (m, 22H, Ar–*H*). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 24.2 (m, N–CH(CH_3)$_2$), 24.9 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.6 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 45.9 (N–CH(CH$_3$)$_2$), 52.9 (CHPh$_2$), 126.5, 127.8, 128.5, 130.4, 136.1, 139.9, 140.9, 145.0 (Ar–*C*). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 78.0. IR ν/cm^{-1} (ATR): 1492 (w), 1446 (m), 1381 (w), 1174 (m), 1114 (w), 942 (m), 835 (w), 732 (w), 696 (s). MS/EI *m*/*z* (%): 497 ($Ar^{\dagger}NP^+$, 69), 167.1 (Ph_2CH^+, 100). Anal. calc. (%) for $C_{47}H_{60}N_3P$ (M_r = 697.99): C, 80.88; H, 8.66; N, 6.02; Found: C, 80.89; H, 8.71; N, 6.08.

Preparation of $Ar^{\dagger}$–N = $PNEt_2$ (4). The ligand $Ar^{\dagger}\{P(NEt_2)_2\}$-NH was deprotonated using $KN(SiMe_3)$ according to a procedure described in the literature, to give $Ar^{\dagger}\{P(NEt_2)_2\}NK(thf)$ (73% yield).[32] A solution of $Ar^{\dagger}\{P(NEt_2)_2\}NK(thf)$ (1.0 g, 1.33 mmol) in toluene (40 ml) was slowly added to a solution of Si_2Cl_6 (0.36 g, 1.33 mmol) in toluene (10 ml) at −80 °C. The reaction mixture was allowed to reach room temperature over a period of 12 hours to furnish a bright yellow solution. The reaction mixture was filtered through a glass fiber pad. All volatile components were removed from the filtrate under reduced pressure and the residue was washed with minimal amounts of hexane. The product was dissolved again in toluene, concentrated and kept at −30 °C to yield bright yellow crystals of **4** (0.40 g, 0.70 mmol). Yield: 53%. M.p.: 137–138 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.60 (m, 3H, –CH_3), 0.92 (m, 3H, CH_3), 1.05 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.53 (m, 2H, N–CH_2–), 2.56 (m, 1H, –CH(CH$_3$)$_3$), 3.38 (m, 2H, N–CH_2–), 5.86 (s, 2H, –CHPh$_2$), 6.97–7.23 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 24.5 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.9 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 38.5 (m, –CH_2–CH_3), 40.3 (d, $^3J_{CP}$ = 38 Hz, P=N–CH_2–), 53.9 (CHPh$_2$), 126.3, 126.7, 128.6, 130.5, 133.0 (d, J_{CP} = 7 Hz), 140.0, 144.8 (d, J_{CP} = 14 Hz), 145.7 (Ar–*C*). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 270.2. IR ν/cm^{-1} (ATR): 1600 (w) 1492 (w), 1464 (m), 1444 (s), 1379 (w), 1322 (m), 1288 (w), 1262 (w), 1206 (m), 1176 (m), 1097 (w), 1075 (m), 1020 (s), 938 (m), 892 (w), 862 (w), 786 (m), 767 (m), 730 (m), 697 (s).

Preparation of $Ar^{\dagger}(PPh_2)N$–$SiCl_3$ (5). A solution of *n*-butyllithium in hexane (4.0 ml, 6.45 mmol) was slowly added to a solution of $Ar^{\dagger}(PPh_2)NH$ (**1**) (4.00 g, 6.14 mmol) in thf (80 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently slowly added to a solution of $SiCl_4$ (1.12 g, 6.60 mmol) in thf (20 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the remaining colorless solid was extracted with toluene. The solvent was removed under reduced pressure and the remaining solid was washed two times with hexane (20 ml). Drying *in vacuo* gave **5** (3.51 g, 4.47 mmol) as a fine colorless powder. Yield: 73%. M.p.: dec. > 181 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.88 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.41 (sept., 1H, $^3J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 6.71 (s, 2H, –CHPh$_2$), 6.59–8.16 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 23.7 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.6 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 51.7 (CHPh$_2$), 126.3, 127.0, 128.3, 129.0 (d, J_{CP} = 8 Hz), 130.2, 130.6, 130.9, 131.2, 135.5 (d, J_{CP} = 28 Hz), 142.6, 143.1 (d, J_{CP} = 5 Hz), 146.8 (Ar–*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K), δ = −29.4 (d, $^2J_{PSi}$ = 17 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 65.7. IR ν/cm^{-1} (ATR): 1599 (w), 1493 (m), 1444 (m), 1435 (m), 1377 (w), 1362 (w), 1249 (w), 1196 (w), 1154 (w), 1114 (m), 1086 (w), 1030 (w), 1001 (w), 969 (w), 949 (s), 917 (w), 872 (w), 817 (m), 742 (m), 696 (s). MS/EI *m*/*z* (%): 785.5 (M^+, 4), 467.4 ($Ar^{\dagger}NH_2^+$, 38), 167.2 (Ph_2CH^+, 31). Anal. calc. (%) for $C_{47}H_{41}Cl_3NPSi$ (M_r =

785.26): C, 71.89; H, 5.92; N, 1.61; Found: C, 71.88; H, 5.21; N, 1.74.

Preparation of Ar†(PPh$_2$)N–SiCl$_2$H (6). A solution of *n*-butyllithium in hexane (1.8 ml, 2.91 mmol) was slowly added to a solution of Ar†(PPh$_2$)NH (**1**) (1.90 g, 2.91 mmol) in diethyl ether (80 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour. All volatiles were removed under reduced pressure. The residue was dissolved in toluene and then slowly added to a solution of HSiCl$_3$ (0.41 g, 3.00 mmol) in toluene (20 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. The reaction mixture was filtered through a glass fiber pad. The solvent was removed from the filtrate under reduced pressure and the remaining solid was washed two times with hexane (20 ml). Drying *in vacuo* gave **6** (0.85 g, 1.08 mmol) as a fine colorless powder. Yield: 31%. M.p.: 168–169 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 296 K), δ = 0.87 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(C*H*$_3$)$_2$), 2.40 (sept., 1H, $^3J_{HH}$ = 7 Hz, –C*H*(CH$_3$)$_2$), 5.12 (s, 1H, $^1J_{SiH}$ = 339 Hz, Si–*H*), 6.70 (s, 2H, –C*H*Ph$_2$), 6.97–8.14 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 76 MHz, 296 K), δ = 23.7 (Ar†–CH(*C*H$_3$)$_2$), 33.6 (Ar†–*C*H(CH$_3$)$_2$), 51.8 (*C*HPh$_2$), 127.7 (d, J_{CP} = 49 Hz), 128.3, 128.6, 128.9 (d, J_{CP} = 8 Hz), 130.0, 130.2, 130.9, 135.3 (d, J_{CP} = 26 Hz), 136.5 (J_{CP} = 24 Hz), 143.1, 143.4 (d, J_{CP} = 4 Hz), 146.5, 147.0 (Ar–*C*). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 80 MHz, 296 K), δ = −23.9 (d, $^1J_{SiH}$ = 339 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 296 K), δ = 63.1. IR ν/cm^{-1} (ATR): 1599 (w), 1492 (m), 1458 (w), 1429 (m), 1380 (w), 1249 (w), 1202 (w), 1154 (w), 1122 (m), 1109 (m), 1029 (w), 998 (w), 922 (m), 867 (m), 831 (m), 765 (w), 744 (s), 696 (s). Anal. calc. (%) for C$_{47}$H$_{42}$Cl$_2$NPSi (M_r = 750.82): C, 75.19; H, 5.64; N, 1.87; Found: C, 75.12; H, 5.70; N, 1.92.

Preparation of Ar†(PPh$_2$)N–SiPh$_2$Cl (7). A solution of *n*-butyllithium in hexane (2.2 ml, 3.45 mmol) was slowly added to a solution of Ar†(PPh$_2$)NH (**1**) (2.14 g, 3.28 mmol) in diethyl ether (80 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently slowly added to a solution of Ph$_2$SiCl$_2$ (0.89 g, 3.50 mmol) in diethyl ether (20 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the remaining colorless solid was extracted with hot toluene. The solvent was removed under reduced pressure and the remaining solid was washed two times with hexane (20 ml). Drying *in vacuo* gave **7** (1.95 g, 2.25 mmol) as a fine colorless powder. Yield: 68%. M.p.: 174–176 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 296 K), δ = 0.96 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(C*H*$_3$)$_2$), 2.51 (sept., 1H, $^3J_{HH}$ = 7 Hz, –C*H*(CH$_3$)$_2$), 6.62 (s, 2H, –C*H*Ph$_2$), 6.75–7.66 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 76 MHz, 296 K), δ = 23.9 (Ar†–CH(*C*H$_3$)$_2$), 33.6 (Ar†–*C*H(CH$_3$)$_2$), 51.3 (*C*HPh$_2$), 125.7, 126.3, 127.9, 128.9, 128.5 (d, J_{CP} = 8 Hz), 129.9, 130.2, 130.3, 130.6, 131.0, 135.0 (d, J_{CP} = 23 Hz), 136.3, 136.8 (d, J_{CP} = 22 Hz), 142.9, 144.2, 145.8, 146.8 (Ar–*C*). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 80 MHz, 296 K), δ = −14.5. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 296 K), δ = 56.8. IR ν/cm^{-1} (ATR): 1492 (w), 1458 (m), 1429 (m), 1377 (w), 1202 (w), 1123 (w), 1109 (m), 1029 (w), 923 (w), 867 (m), 831 (m), 765 (w), 744 (m), 698 (s). MS/EI *m*/*z* (%): 867.7 (M$^+$, 19), 217.1 (Ph$_2$SiCl$^+$, 58), 167.2 (Ph$_2$CH$^+$, 38%). Anal. calc. (%) for C$_{59}$H$_{51}$ClNPSi (M_r = 868.57): C, 81.59; H, 5.92; N, 1.61; Found: C, 81.43; H, 5.87; N, 1.67.

Preparation of Ar†(PPh$_2$)N–SiH$_3$ (8). To a solution of LiAlH$_4$ (0.19 g, 4.97 mmol) in diethyl ether (20 ml) at −20 °C was added a solution of Ar†(PPh$_2$)N–SiCl$_3$ (1.30 g, 1.66 mmol) in diethyl ether (40 ml). The reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the residue was extracted with toluene. The solution was concentrated and kept at −30 °C to give **8** (0.60 g, 0.88 mmol) as colorless crystals. Yield: 53%. M.p.: dec > 164 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 296 K), δ = 0.91 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(C*H*$_3$)$_2$), 2.44 (sept., 1H, $^3J_{HH}$ = 7 Hz, –C*H*(CH$_3$)$_2$), 3.89 (s, 3H, $^1J_{SiH}$ = 218 Hz, Si–*H*), 6.62 (s, 2H, –C*H*Ph$_2$), 6.97–7.95 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 76 MHz, 296 K), δ = 23.9 (Ar†–CH(*C*H$_3$)$_2$), 33.8 (Ar†–*C*H(CH$_3$)$_2$), 51.8 (*C*HPh$_2$), 126.6 (d, J_{CP} = 36 Hz), 128.4, 128.6, 128.7 (d, J_{CP} = 7 Hz), 129.1, 129.9, 130.3, 130.6, 134.2 (d, J_{CP} = 24 Hz), 140.2 (d, J_{CP} = 21 Hz), 143.1 (d, J_{CP} = 4 Hz), 143.7, 146.3 (Ar–*C*). ^{1}H/^{29}Si HMBC NMR (C$_6$D$_6$, 80 MHz, 296 K), δ = −47.1 (d, $^1J_{SiH}$ = 218 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 296 K), δ = 59.6. IR ν/cm^{-1} (ATR): 1598 (w), 1493 (m), 1445 (m), 1381 (w), 1320 (w), 1248 (w), 1206 (w), 1160 (w), 1119 (m), 1089 (m), 1031 (w), 1001 (w), 975 (m), 930 (s), 882 (m), 843 (m), 765 (m), 742 (m), 696 (s). MS/EI *m*/*z* (%): 681.6 (M$^+$, 35), 496.4 (Ar†NP$^+$, 12). Anal. calc. (%) for C$_{47}$H$_{44}$NPSi (M_r = 681.93): C, 82.78; H, 6.50; N, 2.05; Found: C, 82.63; H, 6.64; N, 2.12.

Preparation of Ar†(PPh$_2$)N–Si$_2$Cl$_5$ (9). A solution of *n*-butyllithium in hexane (1.0 ml, 1.61 mmol) was slowly added to a solution of Ar†(PPh$_2$)NH (**1**) (1.00 g, 1.54 mmol) in diethyl ether (40 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour and was subsequently slowly added to a solution of Si$_2$Cl$_6$ (0.45 g, 1.61 mmol) in diethyl ether (10 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed *in vacuo* and the residue was extracted with toluene. The solvent was removed under reduced pressure and the remaining solid was washed two times with hexane (10 ml). Drying *in vacuo* gave **9** (0.94 g, 1.06 mmol) as a fine pale yellow solid. Yield: 66%. M.p.: dec > 138 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 296 K), δ = 0.96 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(C*H*$_3$)$_2$), 2.52 (sept., 1H, $^3J_{HH}$ = 7 Hz, –C*H*(CH$_3$)$_2$), 6.08 (s, 2H, –C*H*Ph$_2$), 6.41–7.53 (m, 32H, Ar–*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 76 MHz, 296 K), δ = 23.9 (Ar†–CH(*C*H$_3$)$_2$), 33.8 (Ar†–*C*H(CH$_3$)$_2$), 52.0 (*C*HPh$_2$), 126.4 (d, J_{CP} = 65 Hz), 128.0, 128.2, 128.5, 129.2 (d, J_{CP} = 9 Hz), 129.6, 130.4 (d, J_{CP} = 30 Hz), 131.3 (d, J_{CP} = 12 Hz), 136.0 (d, J_{CP} = 22 Hz), 142.6, 144.4, 145.3, 146.8 (Ar–*C*). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 80 MHz, 296 K), δ = −29.4 (d, $^2J_{SiP}$ = 62 Hz, –*S*iCl$_2$–), −2.1 (d, $^3J_{SiP}$ = 18 Hz, –*S*iCl$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 296 K), δ = 49.2. IR ν/cm^{-1} (ATR): 1493 (m), 1458 (m), 1434 (m), 1377 (m), 1197 (w), 1157 (m), 1118 (m), 1081 (m), 1031 (w), 949 (m), 917 (w), 866 (w), 814 (m), 763 (w), 745 (s), 696 (s). MS/EI *m*/*z* (%): 167.2 (Ph$_2$CH$^+$, 100). Anal. calc. (%) for C$_{47}$H$_{41}$NCl$_5$PSi$_2$ (M_r =

884.25): C, 63.84; H, 4.67; N, 1.58; Found: C, 63.92; H, 4.57; N, 1.62.

Preparation of $Ar^{\dagger}(PPh_2)N–Si_2H_5$ (10). To a solution of $LiAlH_4$ (0.10 g, 2.54 mmol) in diethyl ether (20 ml) at −20 °C was added a solution of $Ar^{\dagger}(PPh_2)N–Si_2Cl_5$ (0.45 g, 0.51 mmol) in diethyl ether (40 ml). The reaction mixture was allowed to reach room temperature during a period of 12 hours. All volatile components were removed under reduced pressure and the residue was extracted with toluene. The extract was concentrated and kept at −30 °C to give **10** (0.22 g, 0.31 mmol) as colorless crystals. Yield: 61%. M.p.: 176 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.91 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.40 (m, 3H, SiH_3), 2.44 (sept., 1H, $^3J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 4.58 (m, 2H, –SiH_2–), 6.57 (s, 2H, –CHPh$_2$), 6.94–7.91 (m, 32H, Ar–H). ^{1}H/^{29}Si HMBC NMR (C_6D_6, 80 MHz, 296 K), δ = −99.8 (d, $^1J_{SiH}$ = 196 Hz, –SiH_3), −38.6 (d, $^1J_{SiH}$ = 208 Hz, –SiH_2–). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 63.5. IR ν/cm^{-1} (ATR): 2118 (w), 1598 (w), 1492 (m), 1445 (m), 1380 (m), 1200 (w), 1158 (w), 1119 (m), 1088 (m), 1030 (w), 934 (m), 919 (m), 893 (m), 878 (m), 832 (m), 812 (s), 761 (m), 737 (s), 695 (s). MS/EI m/z (%): 452.3 ($Ar^{\dagger+}$, 12), 167.0 (Ph_2CH^+, 81). Anal. calc. (%) for $C_{47}H_{46}NPSi_2$ (M_r = 712.04): C, 79.28; H, 6.51; N, 1.97; Found: C, 79.19; H, 6.62; N, 2.01.

Preparation of $Ar^{\dagger}(PPh_2)N–Si_5Cl_9$ (11). A solution of n-butyllithium in hexane (0.4 ml, 0.60 mmol) was slowly added to a solution of $Ar^{\dagger}(PPh_2)NH$ (**1**) (0.39 g, 0.60 mmol) in diethyl ether (30 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour. All volatiles were removed under reduced pressure. The residue was dissolved in toluene and then slowly added to a solution of Si_5Cl_{10} (0.30 g, 0.61 mmol) in toluene (10 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. The reaction mixture was then filtered through a glass fiber pad. The solvent was then removed from the filtrate under reduced pressure and the remaining solid was washed two times with hexane (10 ml) at 0 °C. Drying *in vacuo* gave **11** (0.35 g, 0.32 mmol) as a pale yellow solid. Yield: 53%. M.p.: dec > 80 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 0.87 (d, 6H, $^3J_{HH}$ = 7 Hz, –CH(CH_3)$_2$), 2.41 (sept., 1H, $^3J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 6.23 (d, 2H, $^5J_{PH}$ = 7 Hz, –CHPh$_2$), 6.36 (s, 2H, Ar–H), 6.83–7.42 (m, 32H, Ar–H). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 23.7 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.5 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 51.6 (CHPh$_2$), 126.1, 127.2, 128.7, 129.3 (d, J_{CP} = 9 Hz), 129.7, 130.3 (d, J_{CP} = 31 Hz), 131.7, 133.0, 135.4 (d, J_{CP} = 18 Hz), 143.4, 144.1, 145.3 (Ar–C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K), δ = −38.2 (d, $^2J_{PSi}$ = 57 Hz), 0.4 (d, $^3J_{PSi}$ = 26 Hz), 1.7 (d, $^4J_{PSi}$ = 4 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 51.9. IR ν/cm^{-1} (ATR): 1493 (w), 1449 (m), 1436 (m), 1385 (w), 1198 (w), 1157 (w), 1120 (m), 1102 (w), 1031 (w), 940 (m), 864 (w), 819 (m), 745 (m), 698 (s). MS/EI m/z (%): 651.5 ($Ar^{\dagger}(PPh_2)NH^+$, 100), 466.3 ($Ar^{\dagger}NH^+$, 42), 167.1 (Ph_2CH^+, 31). Anal. calc. (%) for $C_{47}H_{41}Cl_9NPSi_5$ (M_r = 1110.30): C, 50.84; H, 3.72; N, 1.26; Found: C, 50.83; H, 3.81; N, 1.28.

Preparation of $Ar^{\dagger}\{(PPh_2)N\}_2Si_5Cl_8$ (12). A solution of n-butyllithium in hexane (0.6 ml, 0.96 mmol) was slowly added to a solution of $Ar^{\dagger}(PPh_2)NH$ (**1**) (0.62 g, 0.96 mmol) in diethyl ether (40 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 1 hour. All volatiles were removed under reduced pressure. The residue was dissolved in toluene and was then slowly added to a solution of Si_5Cl_{10} (0.24 g, 0.48 mmol) in toluene (10 ml) at −80 °C. The reaction mixture was allowed to reach room temperature during a period of 12 hours. The reaction mixture was then filtered through a glass fiber pad. The solvent was removed from the filtrate under reduced pressure and the remaining solid was washed two times with hexane (10 ml) at 0 °C. The impure product was dissolved in a minimum amount of toluene and kept at −30 °C to give pale yellow crystals of **12** (0.50 g, 0.29 mmol). Yield: 60%. M.p.: dec > 153 °C. ^{1}H NMR (400 MHz, C_6D_6, 296 K), δ = 1.04 (m, 12H, –CH(CH_3)$_2$), 2.62 (sept., 2H, $^3J_{HH}$ = 7 Hz, –CH(CH$_3$)$_2$), 6.32–7.64 (m, 64H, CHPh$_2$ and Ar–H). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz, 296 K), δ = 23.9 ($Ar^{\dagger}$–CH(CH_3)$_2$), 24.1 ($Ar^{\dagger}$–CH(CH_3)$_2$), 33.9 ($Ar^{\dagger}$–CH(CH$_3$)$_2$), 51.7 (CHPh$_2$), 125.7, 126.1 (d, J_{CP} = 17 Hz), 126.6 (d, J_{CP} = 9 Hz), 126.8, 128.6, 128.8, 129.3, 130.4 (d, J_{CP} = 5 Hz), 130.6, 130.8, 131.2, 135.2, 135.4, 138.0, 143.4 (d, J_{CP} = 34 Hz), 144.3, 144.7 (d, J_{CP} = 20 Hz), 146.0 (d, J_{CP} = 24 Hz), 146.9 (Ar–C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K), δ = −38.3 (d, $^2J_{PSi}$ = 51 Hz), 4.1 (d, $^3J_{PSi}$ = 29 Hz), 9.2 (d, $^4J_{PSi}$ = 19 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 296 K), δ = 42.2 (br). IR ν/cm^{-1} (ATR): 1599 (w), 1492 (m), 1449 (m), 1433 (m), 1378 (w), 1200 (w), 1158 (w), 1120 (m), 1077 (m), 1031 (w), 934 (w), 866 (m), 822 (m), 743 (m), 696 (s). Anal. calc. (%) for $C_{94}H_{82}Cl_8N_2P_2Si_5$ (M_r = 1725.68): C, 65.43; H, 4.79; N, 1.62; Found: C, 65.31; H, 6.85; N, 1.62.

X-ray crystallography

Single crystals of compounds **1**, **2**, **2-K**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements for compounds **1**, **2**, **3**, **5**, **6** and **9** were carried out on either a Bruker X8 Apex and an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å), and for compounds **2-K**, **4**, **7**, **8**, **10**, **11** and **12** the MX1 beamline of the Australian Synchrotron (λ = 0.71090 Å). The software package Blu-Ice[33] was used for synchrotron data acquisition, while the program XDS[34] was employed for synchrotron data reduction. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[35] using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. The asymmetric unit of the crystal structure of compound **8** was found to exhibit site disorder between a 50 : 50 ratio of a molecule of the protonated ligand ($Ar^{\dagger}(PPh_2)NH$) and **8**, sitting on the molecular same site. This disorder was successfully modelled. For the crystal structure of compound **12**, only a low value (20.96°) for Θ_{max} for the diffraction data could be attained. This arose from the data above that angle being too weak to observe. Hence, the software used to integrate the diffraction data at the Australian Synchrotron discarded these data. This resulted in the poor quality of the crystal structure. Although the metrical parameters for the compound should not be considered as accurate, the gross molecular connectivity

of the compound is unambiguous. Crystal data, details of data collections and refinement are given in Table S1 in the ESI.†

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