

Labile Base-Stabilized Silyliumylidene Ions. Non-Metallic Species Capable of Activating Multiple Small Molecules

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Abstract: Several base-stabilized silyliumylidene ions (**2** and **3**) with different ligands were synthesized. Their behaviour appeared strongly dependent on the nature of ligand. Indeed, in contrast to the poorly reactive silyliumylidene ions **3c,d** stabilized by strongly donating ligands (DMAP, NHC), the silylene- and sulfide-supported one (**2-H** and **3a**) exhibits higher reactivity toward various small molecules. Further-

more, their capability to successively activate multiple small molecules was clearly demonstrated by processes involving successive reactions with silane/formamide, CO₂ and H₂. Moreover, HBPIn adduct of **3a** (**8-C**) catalyzes the hydroboration of pyridine. Of particular interest, silylene-supported silyliumylidene complex **2-H** is one of the rare species able to activate two H₂ molecules.

Introduction

The chemistry of main-group element species exhibiting “transition metal-like behavior” has attracted much attention in recent years.^[1] Thus, some important achievements have been reported, including the activation of small molecules such as H₂ by digermynes,^[2] disilenes,^[3] carbenes,^[4] heavier carbene analogues (metallylenes),^[5] frustrated Lewis pairs (FLPs)^[6] and low-valent group 13 species.^[7–10] A significant advance in the field is the use of multi-coordination(reactive)-site species, capable of activating multiple small molecules to carry out successive reactions. However, the number of such non-metallic species still remains limited. The first reported example is a digermine **I**, featuring a reactive Ge≡Ge triple bond, capable of activating two H₂ molecules, and being an efficient catalyst for the [2 + 2 + 2] cyclization of alkynes, highlighting a multi-reactive character (Figure 1).^[11] It has also been shown that metallylenes

II,^[12] Lewis pairs **III**^[13] and FLP **IV**,^[14] with labile hydrogen substituents, are also capable of activating two small molecules, and show particular catalytic activity compared to conventional species. We also recently demonstrated that a stable germylene-B(C₆F₅)₃ complex **V**, which can behave as both an electrophilic germylene and a FLP, is capable of achieving the successive activation of Et₃SiH and CO₂, allowing the selective catalytic hydrosilylation of CO₂.^[15] However, it should be noted that highly active systems able to activate two H₂ molecules are extremely rare and, to the best of our knowledge, the boragermene **XIII**,^[16] and the phosphine-stabilized diborene **XIV**,^[17] described by Kinjo and Braunschweig respectively, are only the examples reported.

In this context, silyliumylidene cations **VI**, presenting mixed silyl cation/silylene functionalities should be interesting candidates as multi-activating systems. Indeed, Müller et al. have recently demonstrated that a transient silyliumylidene ion is able to activate two molecules of benzene, via C–H bond cleavages, at the same silicon site.^[18] Although silyliumylidene cations **VI** are, in general, highly reactive transient species,^[19] they can be stabilized by compensating their electron deficiency at the silicon center either by L-ligands or by π -electron donating substituents. Jutzi et al. have reported the first stable η^5 -silyliumylidene cation **VII** with a half-sandwich structure.^[20] Mono-coordinate Si(II) cation **VIII**, stabilized by π -interaction with aryl groups, has also recently been synthesized by Hinz.^[21] The Driess group^[22] and more recently Aldridge et al.^[23] successfully stabilized two-coordinate silyliumylidene cations **IX** combining both stabilizations (L-ligand and π -donating amino substituent). The multi-reactive character of **IX** was demonstrated by successive reactions with an alkyne and Et₂O.^[24] Furthermore, several base-stabilized silyliumylidene cations **X–XII** have also been isolated as stable complexes with two donating ligands.^[25–27] These well-stabilized three-coordinate silyliumylidene complexes **X–XII** are probably the most appropriate for their practical use. Indeed, So et al. elegantly demonstrated that the NHC-stabilized Si(II) cation **XI** (R=H) is an

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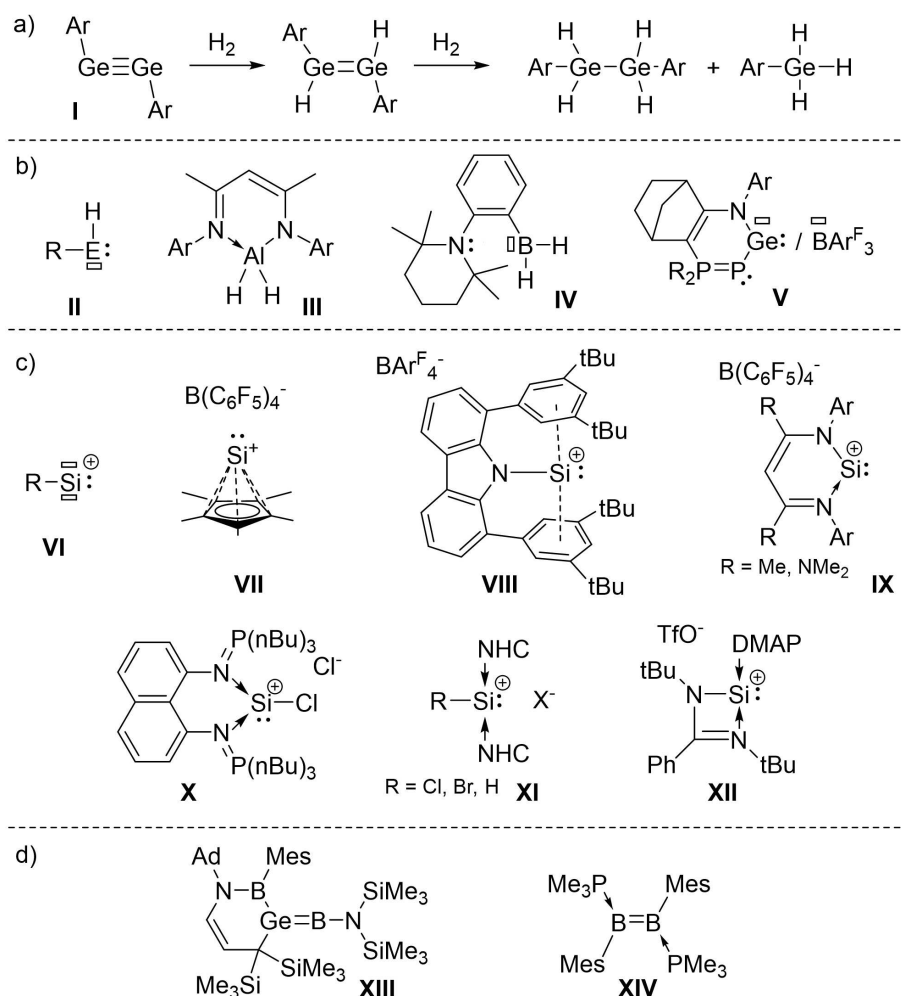


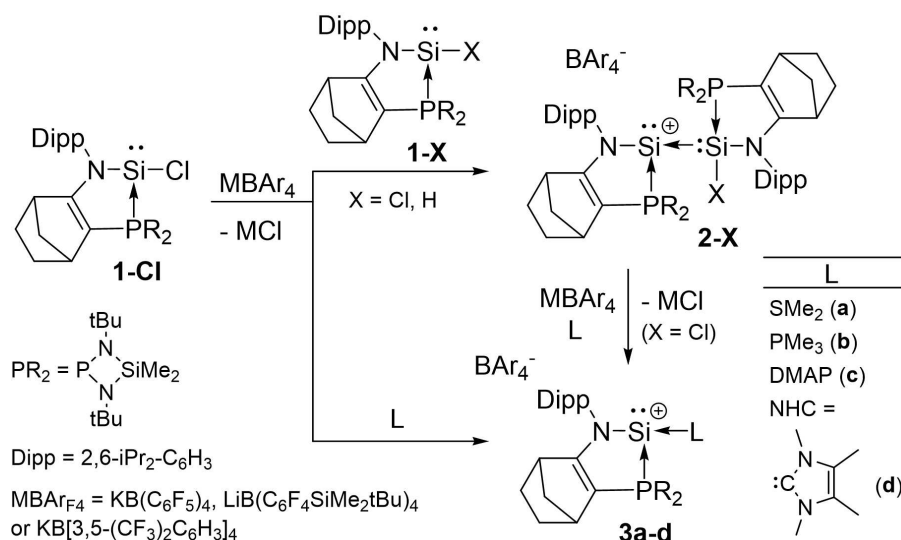
Figure 1. a) Stepwise reactions of digermynes **I** with two H_2 molecules. b) Examples of non-metallic species (**II–V**) able to activate multiple small molecules. c) Donor-supported silyliumylidene ions (**VII–XII**). d) Compounds capable of activating two molecules of H_2 .

efficient catalyst for hydroboration of carbonyl compounds^[28] and N-formylation of amines.^[29] However, the study of the reactivity of these species is still in its infancy,^[26,27] which is partly explained by an excessive stabilization of silicon center by strong electron-donating ligands (NHCs, DMAP, phosphazenes, etc) which considerably reduce their reactivity. Therefore, the use of less coordinating ligands should improve the availability of the two coordination sites on the Si atom and bring out the expected properties as a multi-activation system.

Results and Discussion

We have demonstrated that phosphine-stabilized silylenes **1-X** ($\text{X} = \text{H}, \text{Cl}, \text{Ph}, \text{SnMe}_3$) thanks to the weak coordination of phosphine and particular ligand effect, remain highly reactive species^[30] and present, to some extent, a “transition metal-like behavior”.^[31–33] Thus, we have considered the use of **1-Cl**^[34] as a platform to synthesize new silyliumylidene cations (**2** and **3**) stabilized by two coordinating ligands.

The reaction of chlorosilylene **1-Cl** with half an equivalent of $\text{NaB}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4$ cleanly affords the chlorosilylene-adduct of silyliumylidene ion **2-Cl** (Scheme 1). The same result was obtained even in the presence of an excess of sodium borate salt (5 equiv.). Furthermore, no traces of the expected two-coordinate silyliumylidene ion were detected by NMR, probably due to an excessive electrophilic character. Because **2-Cl** has multiple chiral centers (Si^{II} atom and bicyclic backbone in each $\text{Si}(\text{II})$ -unit), it exists as a mixture of four diastereomers in a 10:3:2:1 ratio, as indicated by four sets of AX-systems observed in the ^{31}P NMR spectrum [68.3/45.1 ppm ($^3J_{\text{PP}} = 37.6$ Hz), 70.3/53.4 ppm ($^3J_{\text{PP}} = 2.6$ Hz), 69.3/54.9 ppm ($^3J_{\text{PP}} = 2.5$ Hz), 69.6/45.2 ppm ($^3J_{\text{PP}} = 32.4$ Hz)]. The ^{29}Si NMR spectrum displays two doublet of doublets for the two central silicon atoms of the major isomer at -13.2 ppm [$J_{\text{SiP}} = 56.0$ and 181.3 Hz ($\lambda^2\sigma^3\text{-Si}$)] and at -18.3 ppm [$J_{\text{SiP}} = 18.9$ and 69.2 Hz ($\lambda^2\sigma^4\text{-Si}$)], respectively. **2-Cl** was isolated as air-sensitive yellow crystals from a saturated fluorobenzene/toluene solution at -30°C (92% yield). Similarly, the reaction of **1-Cl** with $\text{NaB}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4$ in the presence of one equivalent of hydrogenosilylene derivative **1-H** affords the related silylene→silyliumylidene



Scheme 1. The synthesis of donor-stabilized silyliumylidene ions **2-X** ($X=\text{Cl}$, H) and **3a-d**.

complex **2-H** (Scheme 1) as a mixture of only two diastereomers. The structure of **2-H** was confirmed by X-ray diffraction analysis (Figure 2-left). The Si–Si bond length [2.397(1) Å] of **2-H** corresponds to Si–Si single bonds and is longer than those of the reported Lewis base-stabilized disilenes [2.3224(7)–2.3575(8) Å].^[35]

Although all diastereomers of **2-Cl** could not be characterized by NMR spectroscopy due to the complex signal pattern, their formation was indirectly confirmed by a ligand exchange reaction with an excess of non-chiral SMe_2 (5 equiv.) and $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ (1 equiv.) which affords a sulfide-supported silyliumylidene ion **3a** as a single product (Scheme 1). Indeed, the ^{31}P NMR spectrum of the solution mixture shows only one

singlet signal at $\delta = 66.6$ ppm for **3a**. The same product **3a** can be obtained directly by the reaction of chlorosilylene **1-Cl** with 1 equivalent of MBar_4 [$\text{KB}(\text{C}_6\text{F}_5)_4$ or $\text{LiB}(\text{C}_6\text{F}_4\text{SiMe}_2\text{tBu})_4$] in the presence of an excess of SMe_2 ligand (5 equiv.) in $\text{C}_6\text{H}_5\text{F}$ at RT (Scheme 1) and was isolated as air-sensitive yellow crystals in 67% yield. In the ^{29}Si NMR spectrum, **3a** displays a doublet signal at $\delta = -15.7$ ppm with a large Si–P coupling constant ($^1J_{\text{SiP}} = 167.1$ Hz), in the region of that of **2-Cl** (-18.3 ppm, $^1J_{\text{SiP}} = 181.2$ Hz, $^2J_{\text{SiP}} = 55.9$ Hz) (Figure 3) and is only slightly upfield-shifted compared to precursor **1-Cl** (-10.5 ppm). This data is in marked contrast to the case of NHC-stabilized silyliumylidene ions **XI** whose ^{29}Si NMR resonances (-55.3 to -70.9 ppm) are significantly upfield-shifted in comparison to those of the halogenated precursors (-9.7 to 13.8 ppm).^[26a–c] The same upfield-shift trend was also observed in the case of cationic Si(II) complex **XII** (14.6 to -82.3 ppm).^[27,36] As expected, the ^{29}Si chemical shift of **3a** is very different from those of mono-coordinate silyliumylidene cation **VIII** (56.8 ppm),^[21] two-coordinate ones **IX** (69.3 to 80.0 ppm),^[22,23] and the pentamethylcyclopentadienyl-substituted penta-coordinate cation **VII** (-400.2 ppm).^[20] The X-ray structure of **3a** reveals a trigonal pyramidal geometry around Si1 center ($\Sigma^\circ_{\text{Si}} = 285.2^\circ$) with an angle between phosphine and sulfide ligands [$\text{S}–\text{Si}1–\text{P} = 99.1(1)^\circ$] close to 90° (Figure 2-right),^[37] which is in good agreement with an orthogonal interaction of both ligands with the two empty perpendicular 3p-orbitals on Si1 atom. The Si1–S distance [2.334(1) Å] is significantly longer than classical Si–S covalent bonds (2.10–2.15 Å), in agreement with a dative character of the S–Si bond. The Si–P bond length [2.372(1) Å] is similar to that of **1-Cl** (2.35 Å).^[34]

As expected, the same reaction, performed in the presence of more strongly donating ligands such as trimethylphosphine (PMe_3), 4-dimethylaminopyridine (DMAP) or an N-heterocyclic carbene (NHC), results in the quantitative formation of the corresponding silyliumylidene ion complexes **3b–d** (Scheme 1). It is important to note that, **3c,d** can be obtained using NaBPh_4

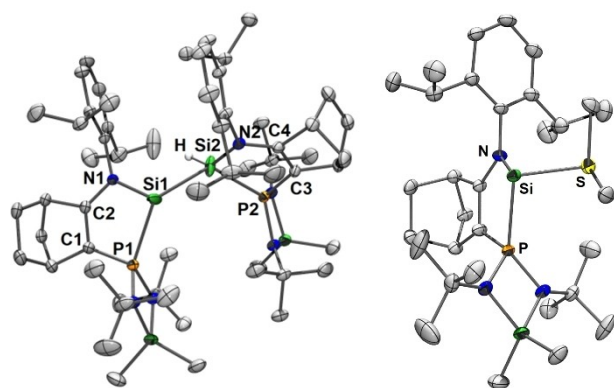
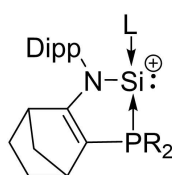


Figure 2. Molecular structure of **2-H** (left) and **3a** (right). Thermal ellipsoids represent 30% probability. Disordered, H atoms and counter anions $\text{B}[\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4^-$ for **2-H** and $\text{B}(\text{C}_6\text{F}_4\text{SiMe}_2\text{tBu})_4^-$ for **3a** are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: **2-H**: Si1–Si2 2.397(1), N1–Si1 1.823(2), Si1–P1 2.335(1), N2–Si2 1.815(2), Si2–P2 2.334(1), N1–Si1–Si2 108.2(1), Si2–Si1–P1 128.8(1), N1–Si1–P1 89.7(1), N2–Si2–Si1 108.5(1), Si1–Si2–P2 126.7(1), N2–Si2–P2 89.9(1). **3a**: Si1–S 2.334(1), Si1–P 2.372(1), N1–Si1 1.818(3), P–C1 1.738(3), C1–C2 1.362(4), C2–N1 1.362(4), Si1–P–C1 91.2(1), P–C1–C2 116.0(2), C1–C2–N1 124.8(3), C2–N1–Si1 114.2(2), N1–Si1–S 98.2(1), N1–Si1–P 87.9(1), S–Si1–P 99.1(1).



L	δ (ppm) [J_{SiP} (Hz)]
1-Cl (2-Cl)	-13.2 [56.0 and 181.3] (major, 63 %) -18.3 [18.9 and 69.2] (minor, 37 %)
1-H (2-H)	-20.8 [24.3 and 226.2] (major, 70 %) -22.5 [22.3 and 227.3] (minor, 30 %)
SMe₂ (3a)	-15.7 [167.0]
PMe₃ (3b)	-44.5 [171.6 and 223.2]
DMAP (3c)	-14.5 [178.4]
NHC (3d)	-26.8 [186.5]

Figure 3. ^{29}Si NMR data (chemical shifts in ppm and Si–P–Coupling constants in Hz) of silyliumylidene ions **2** and **3**.

with a less Lewis acid character at the sodium cation, whereas the more electrophilic **2-X** and **3a** cannot be generated in the same conditions.

To gain more insight into the electronic structure of base-stabilized silyliumylidene ions **2** and **3**, DFT calculations have been performed at the M06-2X/6-31G(d) level of theory. The optimized structure of **3a** agrees quite well with the experimental data (Si–S: 2.389 Å, Si–P: 2.366 Å, Si–N: 1.813 Å). The highest occupied molecular orbital (HOMO) is mainly localized at the silicon center as a lone pair (Figure 4c) and the lowest unoccupied molecular orbitals (LUMO+1 and LUMO) correspond to the two perpendicular anti-bonding σ^* orbitals localized on the Si atom. (a combination of $\sigma^*_{\text{Si-P}}$ and $\sigma^*_{\text{Si-N}}$ for LUMO+1 and $\sigma^*_{\text{Si-S}}$ for LUMO) (Figure 4a, b). As expected, due to the weak coordination of sulfide ligand and the positive charge, both LUMO and HOMO energies (LUMO: -3.41 eV, HOMO: -9.42 eV) are significantly lower than those of the neutral phosphine-stabilized silylene **1-H** ($R=\text{H}$, LUMO: $+0.53$ eV, HOMO: -6.05 eV) and are close to those of the corresponding two-coordinate silyliumylidene complex **4** with only a phosphine ligand (LUMO: -5.15 eV, HOMO: -10.36 eV). Moreover, the LUMO ($\sigma^*_{\text{Si-S}}$) is significantly lower than LUMO+1

($\sigma^*_{\text{Si-P}}$ and $\sigma^*_{\text{Si-N}}$) certainly due to the weaker $\text{Me}_2\text{S} \rightarrow \text{Si}^+$ interaction than $\text{R}_3\text{P} \rightarrow \text{Si}^+$ and $\text{N} \rightarrow \text{Si}^+$. The HOMO–LUMO gap ($\Delta E_{\text{HOMO-LUMO}}$) calculated for **3a** (6.01 eV) is in between those of silylene **1-H** (6.58 eV) and **4** (5.21 eV). Of particular interest, the energy gaps of silylene-stabilized silyliumylidene ions **2-X** ($\Delta E_{\text{HOMO-LUMO}}$: 4.85 eV for **2-Cl**, 5.05 eV for **2-H**) are even smaller than that of two-coordinate silyliumylidene **4** due to the high HOMO energy levels (**2-Cl**: -8.31 eV, **2-H**: -8.21 eV).

Furthermore, the calculated Gibbs free energy for the formation of **3a** by the coordination of sulfide ligand on the two-coordinate silyliumylidene ion **4** ($\Delta G = -8.3$ kcal/mol) is considerably smaller than that of NHC-stabilized **3d** ($\Delta G = -38.0$ kcal/mol, Figure 5). This result is in good agreement with the labile character of dimethylsulfide ligand, and suggests that silyliumylidene ion **3a** should be much more reactive than **3b–d**. Steric reasons certainly explain the low Gibbs energy for the formation of **2-Cl** ($\Delta G_{4 \rightarrow 2\text{-Cl}} = -8.6$ kcal/mol) compared with **3b–d**, while in the case of **2-H** (smaller silylene ligand) this energy is considerably larger ($\Delta G_{4 \rightarrow 2\text{-Cl}} = -18.0$ kcal/mol). The larger Gibbs free energy for the formation of **2-H** can also be due to the stronger donating ability of **1-H** than **1-Cl**.

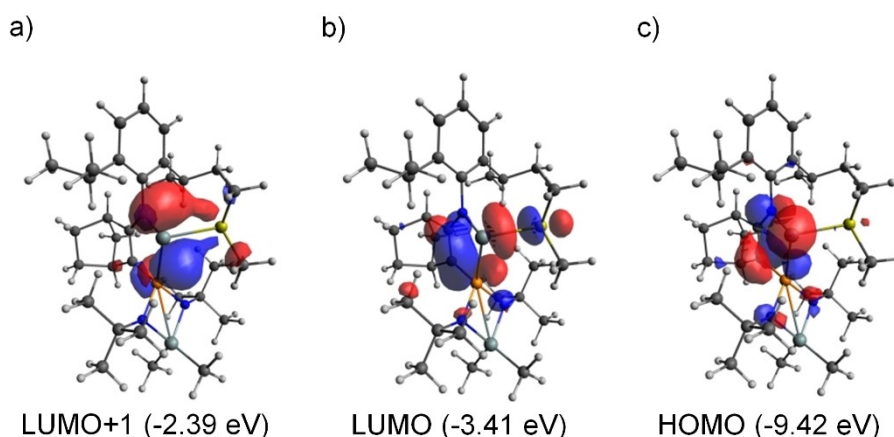


Figure 4. Frontier orbitals of **3a** calculated at the M06-2X/6-31G(d) level (Isosurface level: ± 0.045 e/(a.u.)³).

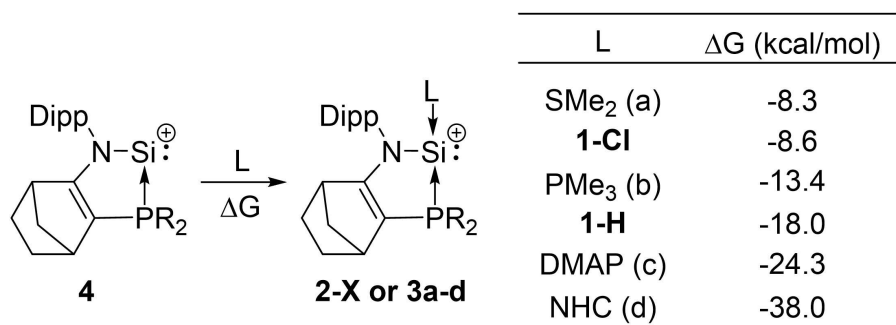
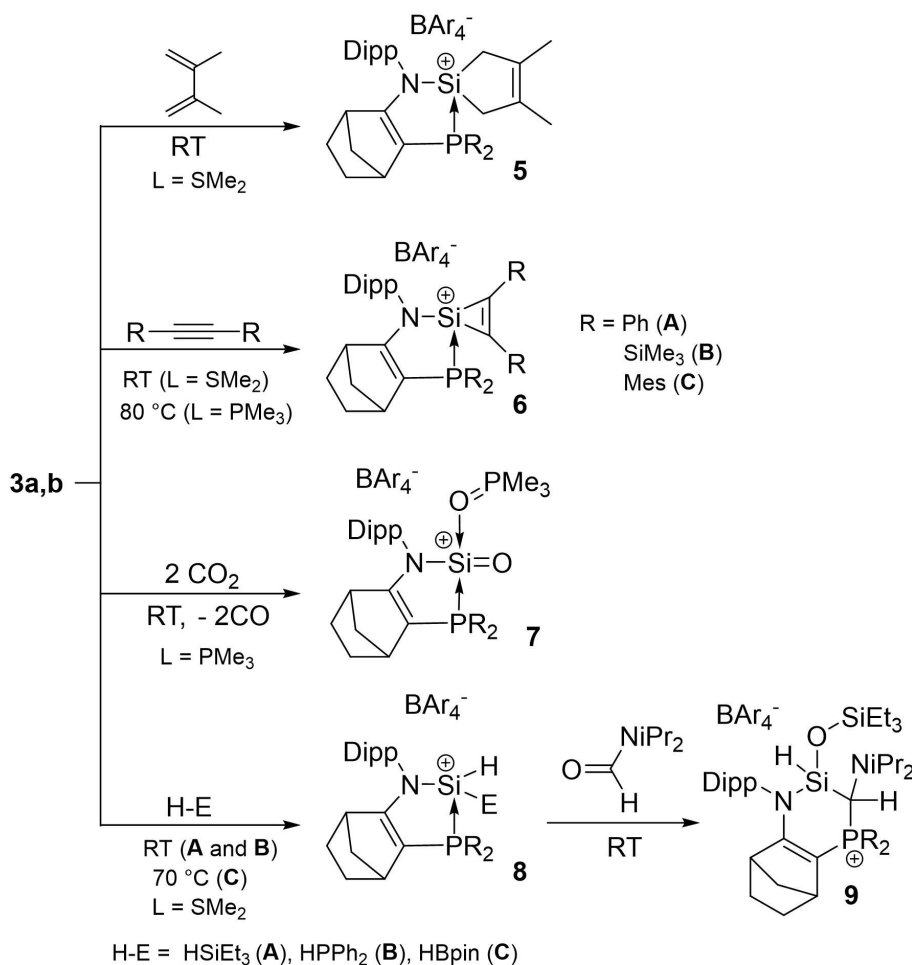


Figure 5. Calculated Gibbs free energy (ΔG in kcal/mol) for the formation of silyliumylidene ions **2-X** and **3a-d** by the reaction of two-coordinate ion **4** with a L-ligand (**1-X**, SMe₂, PMe₃, DMAP or NHC).

As expected, silyliumylidene ion **3a** supported by the weak SMe₂ ligand presents a high reactivity and with 2,3-dimethyl-1,3-butadiene an immediate [4 + 1]-cycloaddition reaction was observed at RT affording the phosphine-stabilized five-membered cyclic silylium ion **5**, and release of sulfide ligand (Scheme 2). The ³¹P NMR signal of **5** (37.6 ppm) is significantly shifted to high field compared to that of **3a** (67.0 ppm). Similar chemical shifts have been previously observed for related

phosphine-stabilized silylium ions (22–40 ppm).^[38] In the case of NHC-stabilized cation **3d**, no reaction was observed even upon heating at 100 °C. Silyliumylidene ion **3a** also immediately reacts with diphenylacetylene to give the corresponding [2 + 1]-cycloadduct **6-A** at RT. The strongly high-field shifted ²⁹Si NMR signal of **6-A** (−96.4 ppm, ¹J_{Si-P} = 186.6 Hz) is in good agreement with the formation of a three-membered cyclic silylium ion.^[24] Here again, **3c, d** do not react with diphenylacetylene at RT,



Scheme 2. The reactions of **3a, b**.

and at 100 °C, a complex mixture of compounds was obtained. The extraordinarily enhanced reactivity of **3a** was also demonstrated by the reactions, at RT, with bulky alkyne derivatives such as bis(trimethylsilyl)- or bis(mesityl)acetylene to give the corresponding silacyclopentenyl cation derivatives **6-B,C**. Both compounds show strongly high-field shifted ^{29}Si NMR signals (**6-B**: -100.1 ppm, $^1J_{\text{Si-P}} = 215.8$ Hz, **6-C**: -86.9 ppm, $^1J_{\text{Si-P}} = 174.2$ Hz). The Me_3P -supported silyliumylidene ion **3b** reacts with bis(trimethylsilyl)acetylene at 80 °C, but, as the reaction progresses, it slows down and almost stops at about 30% of conversion. Probably the increasing amount of released Me_3P inhibits the ligand dissociation from complex **3b**, which hinders the progress of the reaction. Therefore, it is clear that for a reaction to take place, the L-ligand is required to dissociate from the silicon center of **3** to generate a more reactive two-coordinate silyliumylidene **4**, unlike the highly reactive neutral phosphine-stabilized silylenes **1**, which react with acetylenes even at room temperature.^[30] The decreased reactivity of base-stabilized silyliumylidenes **3** compared to the neutral ones **1** is probably due to their reduced nucleophilic character.

The Me_3P -stabilized cation **3b** readily reacts with two molecules of CO_2 to afford the cationic silanone (sila-acylium ion) **7** stabilized by the phosphine fragment and $\text{Me}_3\text{P}=\text{O}$, releasing CO as byproduct (Scheme 2). Although, the NMR characterization was not possible due to the insolubility of **7** in any organic solvent, its structure was confirmed by X-ray diffraction analysis (Figure 6-left). The oxidation of donor-stabilized silyliumylidene ion **XI** by CO_2 to give the correspond-

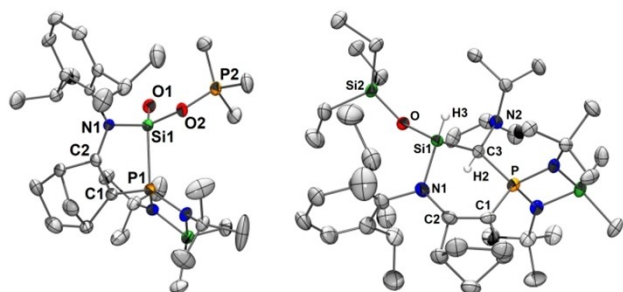


Figure 6. Molecular structures of **7** (left) and **9** (right). Thermal ellipsoids represent 30% probability. Disordered, H atoms (except H2 and H3 for **9**), solvent molecule (**9**) and counter anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: **7**: Si1-O1 1.516(3), Si1-O2 1.708(3), O2-P2 1.560(3), N1-Si1 1.769(4), Si1-P1 2.306(2), Si1-O2-P2 126.0(2), O1-Si1-O2 110.3(2). **9**: N1-Si1 1.781(3), Si1-C3 1.882(5), C3-N2 1.462(5), C3-P 1.842(4), Si1-O 1.608(4), O-Si2 1.666(4), Si1-O-Si2 153.5(5).

ing sila-acylium ion is already known.^[39] Similarly, the reaction probably starts with the oxidation of Si(II) center to generate a cationic silanone **10**, which evolves further by the oxygen transfer from the Si to the P atom of coordinated trimethylphosphine (Figure 7). This process regenerates the cationic Si(II) species **11** which readily undergoes a second oxidation step with CO_2 to give the isolated cationic silanone **7**. It is worth noting that, in this process, the silyliumylidene fragment in **3b** formally behaves as an oxygen transfer catalysts. However, its further catalytic activity was not observed even in the presence of an excess of phosphine (10 equiv.). Probably, the strong $\text{Me}_3\text{P}=\text{O}$ coordination on the Si center in **7** prevents a ligand exchange reaction with Me_3P to reform complex **10**.

Furthermore, **3a** immediately reacts with triethylsilane at RT, via oxidative addition at the Si(II) center, to give the corresponding silylium ion **8-A** (Scheme 2). Similar oxidative additions were observed with diphenylphosphine at RT or H-Bpin at 70 °C affording the corresponding adducts **8-B,C**. These compounds **8-A,B,C** have been fully characterized by NMR spectroscopy (Figure 8) and particularly the Si-H moiety shows a characteristic signal in the ^1H NMR spectra (5.29–5.77 ppm) with large silicon-proton coupling constants ($^1J_{\text{SiH}} = 184.9$ –233.6 Hz).

Of particular interest, silyl-substituted silylium ion **8-A** reacts further with *N,N*-diisopropylformamide, via the cleavage of C=O double bond of amide, to form siloxane derivative **9** (Scheme 2). **9** was isolated as yellow crystals in good yield (85%) and its structure was confirmed by X-ray diffraction analysis (Figure 6-right). The formation of **9** can be explained by the evolution of the silylium-amide complex **12**, via a reductive elimination^[33] to generate a pair of [phosphine-stabilized silylene and a O-silylated iminium cation] **13** which evolves via the silylene insertion into C–O bond of iminium salt^[40] to give the corresponding siloxane substituted iminium cation **14** (Figure 9). **14** undergoes a ring-extension via a 1,2-phosphine ligand migration toward iminium carbon to afford the experimentally obtained **9**.

Interestingly, silylium ion **8-C** ($\text{E}=\text{BPin}$) turns out to be an active catalyst for the hydroborylation of pyridine (Figure 10a).^[41] Indeed, the reaction proceeds at 60 °C in the presence of **8-C** (10 mol%) and is completed in 11 h. Since NMR monitoring of the reaction detected the transient formation of pyridine-supported borenium salt **19** (^{11}B NMR: $\delta = 6.6$ ppm)^[42] and borylsilane derivative **20** [^{31}P NMR: $\delta = 108.5$ ppm (t), $^2J_{\text{PH}} = 20.4$ Hz],^[32] the catalysis cycle probably starts with the reaction

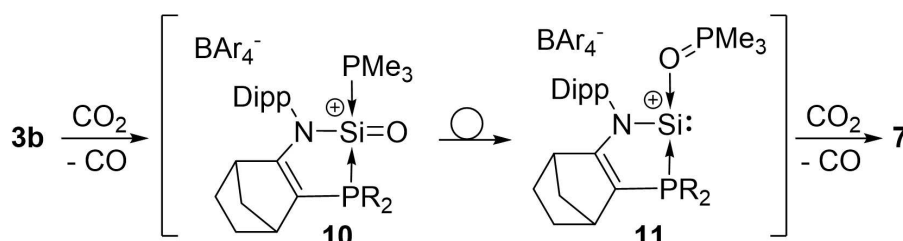
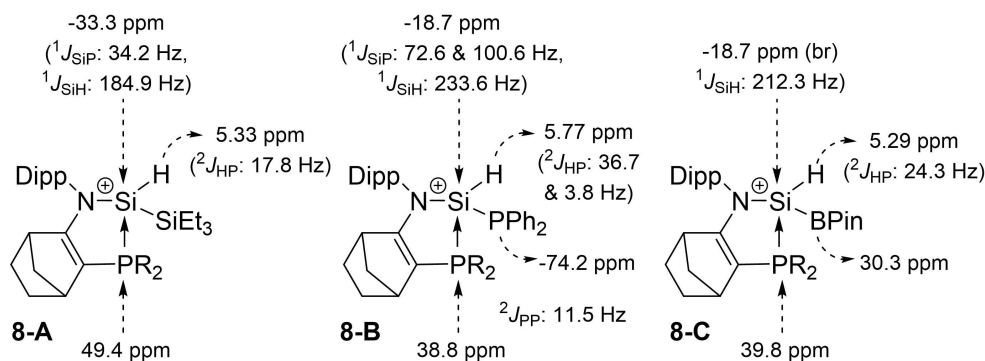
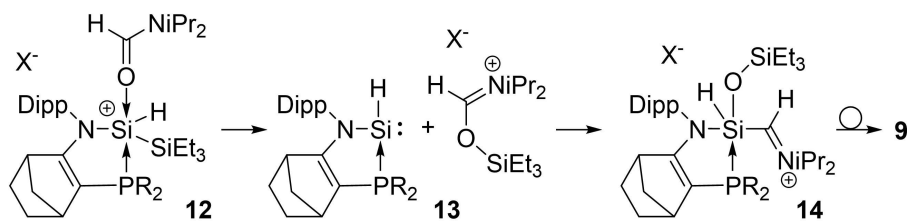
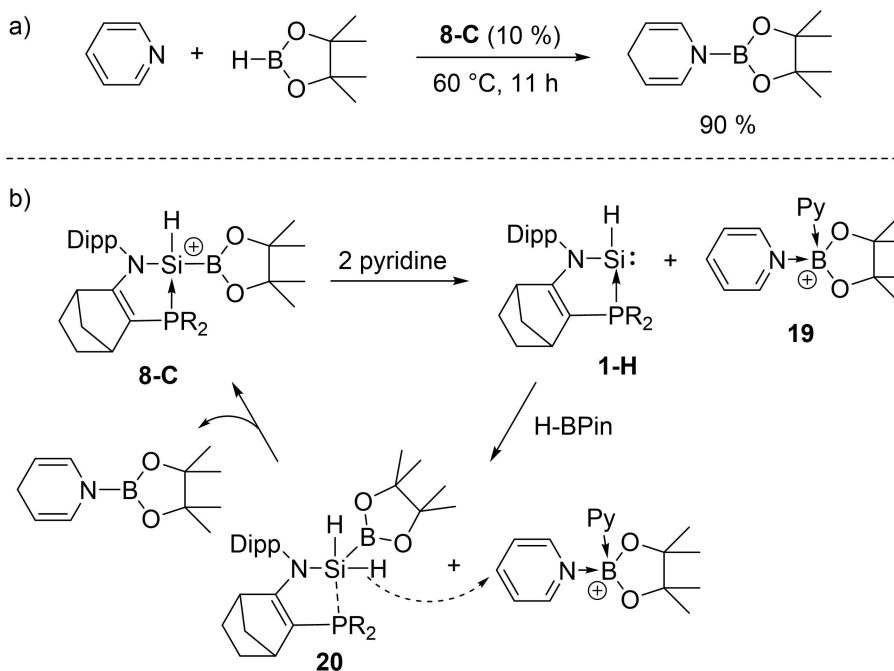


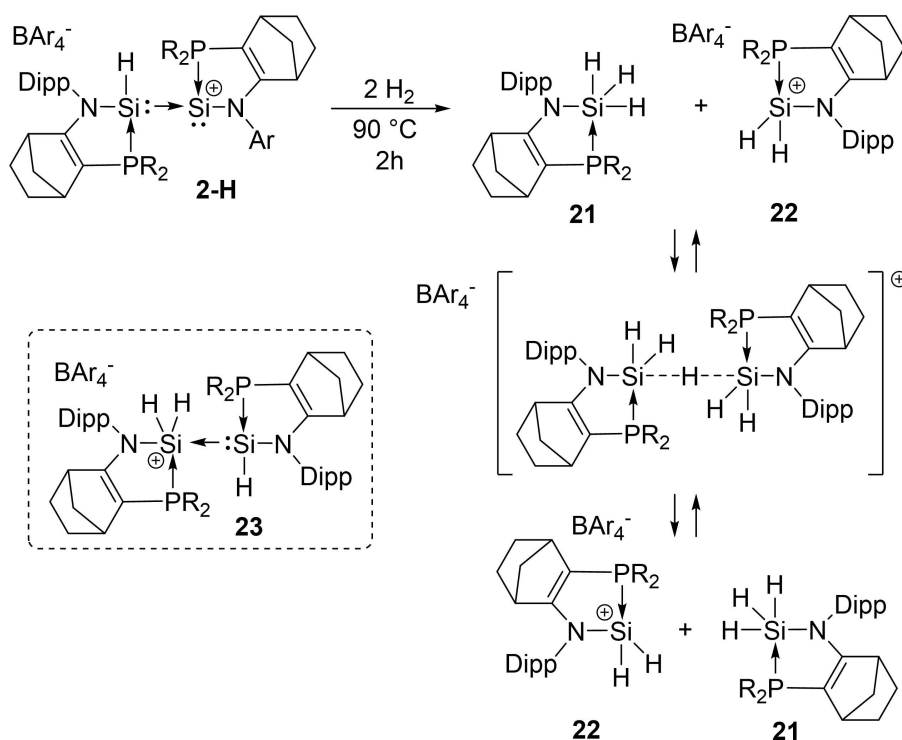
Figure 7. Proposed mechanism of the reaction of **3b** with CO_2 .

Figure 8. NMR data (^1H , ^{11}B , ^{29}Si and ^{31}P) of **8-A**, **B**, **C**.Figure 9. Proposed mechanism for the formation of **9**.Figure 10. Hydroboration of pyridine catalyzed by **8-C** and its proposed mechanism.

of **8-C** with pyridine to generate the hydrogenosilylene **1-H** and the borenium cation **19** (Figure 10b). **1-H** then reacts with H-BPin via oxidative addition to form the detected borylsilane **20**. Hydride transfer from **20** to the borenium-activated pyridine in **19**, which may be promoted by phosphine coordination at

the Si center, completes the catalytic cycle to give the borylamine and regenerated **8-C**.

In contrast to silyliumylidene ions **3a,b**, **2-H** reacts with H_2 (5 bars) at 80°C , leading to the clean formation of trihydrogenosilane **21** and the phosphine-stabilized dihydrogenosilylium ion **22** (Scheme 3). In the ^{31}P NMR spectrum, quartet and triplet



Scheme 3. The double H_2 activation by **2-H** through the intermediacy of mono- H_2 -adduct **23**.

signals were observed for **21** [107.1 ppm (*q*), $^2J_{\text{PH}} = 29.8$ Hz] and **22** [34.0 ppm (*t*), $^2J_{\text{PH}} = 29.2$ Hz], respectively. The ^{29}Si NMR spectrum displays doublet signals for **21** (−43.1 ppm, $^1J_{\text{SiP}} = 19.0$ Hz) and **22** (−78.2 ppm, $^1J_{\text{SiP}} = 202.4$ Hz), which are correlated with ^1H NMR signals at $\delta = 5.10$ ppm ($^2J_{\text{HP}} = 45.2$ Hz) and $\delta = 5.11$ ppm ($^2J_{\text{HP}} = 26.4$ Hz) with ^{29}Si -satellite signals showing a large silicon-hydrogen coupling constant ($^1J_{\text{SiH}} = 267.1$ Hz for **21**, and $^1J_{\text{SiH}} = 261.7$ Hz for **22**). These results indicate the presence of two additional H atoms at the Si atom of each fragment and are in good agreement with the behavior of **2-H** as a multi-functional FLP system able to activate two molecules of H_2 . Both compounds **21** and **22** have been successfully separated: i) by extraction with pentane in the case of neutral silane **21** (60%), and ii) by crystallization from a Et_2O /pentane solution at -30°C in the case of cationic silylium **22** (96%).

The two H_2 -activations probably proceed step-by-step via the transient formation of silylium-silylene complex **23**, generated by the first H_2 activation by **2-H**. The role of each Si center in **23** (Lewis acid/Lewis base) switches from that in **2-H** upon reacting with H_2 . Although the reaction of **2-Cl** with H_2 starts at lower temperature (70°C), the reaction leads to a complicated mixture of compounds. The higher reactivity of **2** compared to **3a,b** can be attributed to the more strongly nucleophilic silylene counterpart, which promotes better FLP-type reactions.^[43] These results also demonstrated that, despite the moderate electrophilic character of phosphine-stabilized silylium ion,^[38] with an appropriate nucleophilic partner, it can form an efficient FLP able to activate H_2 in relatively mild conditions.

The ^{31}P NMR spectrum of the solution mixture of **21** and **22** at RT reveals very broad signals which become sharp upon

lowering the temperature (-60°C). Since the ^{31}P NMR spectra of isolated compounds are well defined at RT, the NMR line broadening observed at RT for the mixture could be explained by a hydride transfer from **21** to **22**, probably being assisted by the P→Si interaction. This supports our hypothesis on the reduction of borenium-activated pyridine **19** by the hydride donation of phosphine-coordinated borylsilane **20** (Figure 10b). In addition, no dehydrogenation reaction (giving back either **23** or **2-H**) was observed by heating a PhF solution of **21** and **22** at 100°C or under vacuum.

Conclusion

In conclusion, we have synthesized and isolated base-stabilized silyliumylidene ions (**2** and **3**) with different ligands. Their behaviour appeared strongly dependent on the nature of ligand. Indeed, in contrast to the poorly reactive silyliumylidene complexes **3c,d** with strongly donating ligands (DMAP, NHC), the dimethylsulfide-supported one **3a** (SMe_2) exhibits higher reactivity toward various small molecules. Furthermore, the potential of **2** and **3** as multi-activating systems was clearly demonstrated by successive reactions with different small molecules such as silane/formamide, CO_2 and H_2 . Moreover, HBPIn adduct of **3a** (**8-C**) catalyzes the hydroboration of pyridine. Of particular interest, silyliumylidene-silylene complex **2-H** is one of the very rare species able to activate two H_2 molecules. Applications of their unique behaviour in catalysis are under active investigations.

Experimental Section

General

All manipulations were performed under inert atmosphere of argon by using Schlenk or high-pressure NMR tube techniques. Dry, oxygen-free solvents were employed. ^1H , ^{11}B , ^{19}F , ^{13}C , ^{29}Si and ^{31}P NMR spectra were recorded on Bruker Avance II 300 MHz, Avance III HD 400 MHz and Avance I and II 500 MHz spectrometers. ^1H , ^{29}Si and ^{13}C NMR chemical shifts are reported in ppm relative to SiMe_4 as internal standard. ^{31}P NMR chemical shifts are expressed in ppm relative to 85% H_3PO_4 . ^{11}B chemical shifts are relative to $\text{BF}_3\cdot\text{OEt}_2$ and ^{19}F chemical shifts are relative to CFCl_3 as external reference. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^1H and ^{13}C resonance signals were attributed by means of 2D COSY, HSQC and HMBC experiments. GC-MS analyses were performed on a MS Perkin Elmer Clarus MS560 and GC PerkinElmer Clarus 500. The phosphine-stabilized silylenes **1-Cl**^[34] and **1-H**^[12a] were synthesized as previously reported.

Syntheses

Compound 2-Cl: In a Schlenk tube, to a mixture of **1-Cl** (850 mg, 1.42 mmol) and $\text{NaBAR}_4^{\text{F}}$ (515 mg, 0.58 mmol, 0.4 equiv), 8 mL of fluorobenzene was added at ambient temperature. After 1 h, precipitated salts were removed by filtration. To this mixture, toluene (ca. 20 mL) was added. **2-Cl** was obtained as orange crystals at -30°C (1.04 g, 92%). Mp. $139\text{--}142^\circ\text{C}$ (decomp.). **2-Cl** is soluble only in polar solvents and decomposes in CDCl_3 and CD_2Cl_2 . Due to the solvent signal ($\text{C}_6\text{H}_5\text{F}$), aromatic region of ^1H NMR were not fully assigned. (Major isomer-A, 59%): ^1H NMR (400 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 0.28$ (s, 3H, SiMe_2), 0.33 (s, 6H, SiMe_2), 0.36 (s, 3H, SiMe_2), 0.61 (s, 9H, CH_3tBu), 0.67 (s, 9H, CH_3tBu), 0.90 (d, $J_{\text{HH}} = 6.1$ Hz, 3H, CH_3Pr), 0.95 (d, $J_{\text{HH}} = 6.1$ Hz, 3H, CH_3Pr), 0.97 (d, $J_{\text{HH}} = 6.5$ Hz, 3H, CH_3Pr), 1.00 (d, $J_{\text{HH}} = 6.5$ Hz, 3H, CH_3Pr), 1.03 (m, 1H, CH_2Norb), 1.06 (m, 1H, CH_2Norb), 1.16 (s, 9H, CH_3tBu), 1.20 (s, 9H, CH_3tBu), 1.20 (overlapped, 3H CH_3Pr), 1.23 (overlapped, 3H CH_3Pr), 1.28 (overlapped, 6H, CH_3Pr), 1.38 (m, 3H, CH_2Norb), 1.52 (m, 3H, CH_2Norb), 1.98 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 2.11 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 2.58 (br m, 1H, CH_{Pr}), 2.88 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 2.88 (overlapped, 2H, CH_{Pr}), 2.95 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.00 (overlapped, 1H, CH_{Pr}), 7.54 (s, 4H, P- CH_{BAR}), 8.38 (s, 8H, $m\text{-CH}_{\text{BAR}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 2.9$ (d, $J_{\text{CP}} = 2.2$ Hz, SiMe_2), 4.5 (d, $J_{\text{CP}} = 1.3$ Hz, SiMe_2), 5.6 (SiMe_2), 6.6 (d, $J_{\text{CP}} = 1.3$ Hz, SiMe_2), 22.7 (CH_3Pr), 22.9 (CH_3Pr), 24.5 (CH_3Pr), 24.8 (CH_3Pr), 25.9 (CH_3Pr), 26.1 (CH_2Norb), 26.5 (CH_2Norb), 26.6 (CH_3Pr), 27.3 (CH_3Pr), 27.5 (CH_3Pr), 27.7 (CH_3Pr), 27.8 (CH_3Pr), 28.1 (CH_2Norb), 28.4 (CH_{Pr}), 28.5 (CH_2Norb), 28.7 (CH_{Pr}), 32.4 (d, $J_{\text{CP}} = 2.1$ Hz, CH_3tBu), 32.5 (d, $J_{\text{CP}} = 1.9$ Hz, CH_3tBu), 33.1 (d, $J_{\text{CP}} = 7.3$ Hz, CH_3tBu), 33.1 (d, $J_{\text{CP}} = 4.6$ Hz, CH_3tBu), 40.7 ($\text{CH}_{\text{bridgehead}}$), 41.2 ($\text{CH}_{\text{bridgehead}}$), 44.3 (d, $J_{\text{CP}} = 13.4$ Hz, $\text{CH}_{\text{bridgehead}}$), 45.6 (d, $J_{\text{CP}} = 10.2$ Hz, $\text{CH}_{\text{bridgehead}}$), 47.8 (d, $J_{\text{CP}} = 3.9$ Hz, CH_2Norb), 50.2 (d, $J_{\text{CP}} = 3.0$ Hz, CH_2Norb), 51.0 (C_{tBu}), 51.7 (C_{tBu}), 52.7 (C_{tBu}), 53.3 (C_{tBu}), 98.7 (dd, $J_{\text{CP}} = 1.7$ and 58.0 Hz, $\text{NC}=\text{CP}$), 105.5 (dd, $J_{\text{CP}} = 4.1$ and 46.7 Hz, $\text{NC}=\text{CP}$), 118.0 (br, P- CH_{BAR}), 124.7 (CH_{Ar}), 125.3 (q, $J_{\text{CF}} = 272.4$ Hz, CF_3), 125.5 (CH_{Ar}), 126.0 (CH_{Ar}), 126.2 (CH_{Ar}), 128.3 (CH_{Ar}), 128.5 (CH_{Ar}), 129.9 (qq, $J_{\text{CF}} = 29.5$ Hz, $J_{\text{CB}} = 2.4$ Hz, $m\text{-C}_{\text{BAR}}$), 135.4 ($o\text{-CH}_{\text{BAR}}$), 137.9 (N-C_{Ar}), 139.0 (N-C_{Ar}), 147.2 (iPr- C_{Ar}), 147.3 (iPr- C_{Ar}), 147.6 (iPr- C_{Ar}), 147.9 (iPr- C_{Ar}), 163.2 (q, $J_{\text{CB}} = 49.6$ Hz, $isoprop\text{-C}_{\text{BAR}}$), 181.8 (d, $J_{\text{CP}} = 34.7$ Hz, $\text{NC}=\text{CP}$), 190.0 (dd, $J_{\text{CP}} = 28.3$ Hz, $\text{NC}=\text{CP}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 45.1$ (d, $J_{\text{PP}} = 37.6$ Hz, P-Si $^+$), 68.3 (d, $J_{\text{PP}} = 37.6$ Hz, P-Si-Cl). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 19.9$ (d, $J_{\text{SiP}} = 2.5$ Hz, SiMe_2), 12.3 (d, $J_{\text{SiP}} = 2.6$ Hz, SiMe_2), -13.2 (dd, $J_{\text{SiP}} = 56.0$ and 181.3 Hz, P-Si-Cl). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 25°C , Ph-F/ C_6D_6): $\delta = -6.0$ (BAR_4). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 25°C , Ph-F/ C_6D_6): $\delta = -62.4$ (CF_3). (Minor isomer-B, 19%): $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph-F/Tol- d_8):

$\delta = 53.4$ (d, $J_{\text{PP}} = 2.6$ Hz, P-Si $^+$), 70.3 (d, $J_{\text{PP}} = 2.3$ Hz, P-Si-Cl). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 19.9$ (d, $J_{\text{SiP}} = 2.5$ Hz, SiMe_2), 12.3 (d, $J_{\text{SiP}} = 2.6$ Hz, SiMe_2), -13.2 (dd, $J_{\text{SiP}} = 56.0$ and 181.3 Hz, P-Si-Cl). (Minor isomer-C, 15%): $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 54.9$ (d, $J_{\text{PP}} = 2.5$ Hz, Si $^+$), 69.3 (d, $J_{\text{PP}} = 2.5$ Hz, P-Si-Cl). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 19.9$ (d, $J_{\text{SiP}} = 2.5$ Hz, SiMe_2), 12.3 (d, $J_{\text{SiP}} = 2.6$ Hz, SiMe_2), -13.2 (dd, $J_{\text{SiP}} = 56.0$ and 181.3 Hz, P-Si-Cl). (Minor isomer-D, 7%): $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 45.2$ (d, $J_{\text{PP}} = 32.4$ Hz, P-Si $^+$), 69.6 (d, $J_{\text{PP}} = 32.4$ Hz, P-Si-Cl).

Compound 2-H: In a Schlenk tube, to a mixture of **1-Cl** (300 mg, 0.533 mmol), **1-H** (340 mg, 0.646 mmol, 1.2 Equation) and $\text{NaBAR}_4^{\text{F}}$ (470 mg, 0.533 mmol), 6 mL of fluorobenzene was added at ambient temperature. After 30 minutes, 3 mL of pentane was added to this mixture and then filtered to remove the precipitates. To this mixture, additional pentane (6 mL) was added to obtain **2-H** as orange crystals (960 mg, 93%). Crystals suitable for X-ray diffraction analysis were obtained from saturated toluene solution at room temperature. Mp. $160\text{--}162^\circ\text{C}$ (decomp.). (Major isomer, 70%): ^1H NMR (400 MHz, -30°C , Ph-F/Tol- d_8): $\delta = -0.04$ (d, $J_{\text{HH}} = 6.6$ Hz, 3H, CH_3Pr), 0.09 (d, $J_{\text{HH}} = 6.9$ Hz, 3H, CH_3Pr), 0.38 (s, 6H, SiMe_2), 0.42 (s, 6H, SiMe_2), 0.94 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH_3Pr), 0.94 (overlapped, 2H, CH_2Norb), 0.96 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH_3Pr), 1.05 (s, 9H, CH_3tBu), 1.06 (overlapped, 2H, CH_2Norb), 1.07 (overlapped, 6H, CH_3Pr), 1.18 (s, 18H, CH_3tBu), 1.22 (s, 9H, CH_3tBu), 1.22 (overlapped, 2H, CH_2Norb), 1.24 (d, $J_{\text{HH}} = 7.0$ Hz, 3H, CH_3Pr), 1.36 (d, $J_{\text{HH}} = 6.5$ Hz, 3H, CH_3Pr), 1.36 (m, 1H, CH_{Pr}), 1.55 (m, 5H, CH_2Norb), 1.91 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 1.96 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 2.39 (d, $J_{\text{HH}} = 6.9$ Hz, 1H, CH_{Pr}), 2.59 (d, $J_{\text{HH}} = 6.5$ Hz, 1H, CH_{Pr}), 2.90 (d, $J_{\text{HH}} = 7.0$ Hz, 1H, CH_{Pr}), 2.92 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.06 (d, $J_{\text{HH}} = 6.8$ Hz, 1H, CH_{Pr}), 3.09 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 5.58 (d, $J_{\text{HP}} = 21.5$ Hz, Si-satellite : $J_{\text{HSi}} = 184.3$ Hz, 1H, Si-H), 7.55 (s, 4H, P- CH_{BAR}), 8.38 (s, 8H, $m\text{-CH}_{\text{BAR}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 3.7$ (d, $J_{\text{CP}} = 3.4$ Hz, SiMe_2), 4.2 (d, $J_{\text{CP}} = 3.6$ Hz, SiMe_2), 5.2 (d, $J_{\text{CP}} = 1.2$ Hz, SiMe_2), 5.2 (d, $J_{\text{CP}} = 3.0$ Hz, SiMe_2), 23.5 (CH_3Pr), 24.0 (CH_3Pr), 24.8 (CH_3Pr), 25.0 (CH_3Pr), 25.3 ($2\times\text{CH}_3\text{Pr}$), 25.5 (CH_2Norb), 26.1 (CH_3Pr), 26.2 (CH_2Norb), 26.5 (CH_3Pr), 27.9 (CH_2Norb), 28.1 (CH_{Pr}), 28.3 (CH_{Pr}), 28.3 (CH_2Norb), 28.6 (CH_{Pr}), 29.7 (CH_{Pr}), 32.2 (d, $J_{\text{CP}} = 6.0$ Hz, CH_3tBu), 32.5 (d, $J_{\text{CP}} = 6.2$ Hz, CH_3tBu), 32.8 (d, $J_{\text{CP}} = 6.6$ Hz, CH_3tBu), 33.1 (d, $J_{\text{CP}} = 5.5$ Hz, CH_3tBu), 42.7 ($\text{CH}_{\text{bridgehead}}$), 43.4 (d, $J_{\text{CP}} = 3.0$ Hz, $\text{CH}_{\text{bridgehead}}$), 44.5 (d, $J_{\text{CP}} = 11.9$ Hz, $\text{CH}_{\text{bridgehead}}$), 45.1 (d, $J_{\text{CP}} = 10.9$ Hz, $\text{CH}_{\text{bridgehead}}$), 48.1 (d, $J_{\text{CP}} = 3.3$ Hz, CH_2Norb), 48.6 (d, $J_{\text{CP}} = 4.8$ Hz, CH_2Norb), 52.7 (C_{tBu}), 52.8 (C_{tBu}), 53.0 (C_{tBu}), 53.1 (d, $J_{\text{CP}} = 0.8$ Hz, C_{tBu}), 98.9 (d, $J_{\text{CP}} = 60.3$ Hz, $\text{NC}=\text{CP}$), 103.5 (d, $J_{\text{CP}} = 49.2$ Hz, $\text{NC}=\text{CP}$), 118.0 (br sept, $J_{\text{CF}} = 3.1$ Hz, P- CH_{BAR}), 124.8 (CH_{Ar}), 125.1 (CH_{Ar}), 125.2 (CH_{Ar}), 125.4 (q, $J_{\text{CF}} = 272.4$ Hz, CF_3), 125.4 (CH_{Ar}), 128.6 (CH_{Ar}), 129.6 (CH_{Ar}), 129.9 (qq, $J_{\text{CF}} = 27.0$ Hz, $J_{\text{CB}} = 2.6$ Hz, $m\text{-C}_{\text{BAR}}$), 135.5 ($o\text{-CH}_{\text{BAR}}$), 137.9 ($2\times\text{N-C}_{\text{Ar}}$), 146.5 (iPr- C_{Ar}), 146.6 (iPr- C_{Ar}), 147.6 (iPr- C_{Ar}), 148.0 (iPr- C_{Ar}), 163.2 (q, $J_{\text{CB}} = 49.7$ Hz, $isoprop\text{-C}_{\text{BAR}}$), 178.8 (d, $J_{\text{CP}} = 31.8$ Hz, $\text{NC}=\text{CP}$), 189.4 (dd, $J_{\text{CP}} = 27.1$ Hz, $\text{NC}=\text{CP}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 53.0$ (d, $J_{\text{PP}} = 35.6$ Hz, P-Si-H), 73.9 (d, $J_{\text{PP}} = 35.6$ Hz, P-Si $^+$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 19.4$ (d, $J_{\text{SiP}} = 5.6$ Hz, SiMe_2), 11.9 (d, $J_{\text{SiP}} = 5.4$ Hz, SiMe_2), -20.8 (dd, $J_{\text{SiP}} = 24.3$ and 226.2 Hz, P-Si $^+$), -23.0 (t, $J_{\text{SiP}} = 11.7$ Hz, P-SiH). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, -30°C , Ph-F/Tol- d_8): $\delta = -5.9$ (BAR). ^{19}F (470 MHz, 25°C , Ph-F/ C_6D_6): $\delta = -62.3$ (CF_3). (Minor isomer, 30%): ^1H NMR (400 MHz, -30°C , Ph-F/Tol- d_8): 5.58 (d, $J_{\text{HP}} = 22.3$ Hz, Si-satellite : $J_{\text{HSi}} = 180.0$ Hz, 1H, Si-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30°C , Ph-F/Tol- d_8): $\delta = 3.7$ (d, $J_{\text{CP}} = 3.6$ Hz, SiMe_2), 4.0 (d, $J_{\text{CP}} = 2.4$ Hz, SiMe_2), 24.1 (CH_3Pr), 24.9 (CH_3Pr), 25.0 (CH_3Pr), 25.4 (CH_3Pr), 25.6 (CH_2Norb), 25.7 (CH_3Pr), 25.9 (CH_2Norb), 26.7 (CH_3Pr), 27.0 (CH_2Norb), 28.0 (CH_{Pr}), 28.2 (CH_2Norb), 29.0 (CH_{Pr}), 42.8 ($\text{CH}_{\text{bridgehead}}$), 52.5 (C_{tBu}), 52.7 (C_{tBu}), 52.9 (C_{tBu}), 101.8 (d, $J_{\text{CP}} = 56.9$ Hz, $\text{NC}=\text{CP}$), 106.7 (d, $J_{\text{CP}} = 20.8$ Hz, $\text{NC}=\text{CP}$), 124.7 (CH_{Ar}), 125.7 (CH_{Ar}), 125.8 (CH_{Ar}), 128.7 (CH_{Ar}), 129.5 (CH_{Ar}), 146.4 (iPr- C_{Ar}), 147.5 (iPr- C_{Ar}), 148.3 (iPr- C_{Ar}), 178.5 (d, $J_{\text{CP}} = 31.4$ Hz, $\text{NC}=\text{CP}$), 191.5 (dd, $J_{\text{CP}} = 26.2$ Hz,

NC=CP). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30°C , Ph–F/Tol- d_8): $\delta = 51.2$ (d, $J_{\text{PP}} = 39.6$ Hz, P–Si–H), 71.7 (d, $J_{\text{PP}} = 39.6$ Hz, P–Si $^+$). ^{31}P NMR (162 MHz, -30°C , Ph–F/Tol- d_8): $\delta = 51.2$ (dd, $J_{\text{PH}} = 21.8$ Hz, $J_{\text{PP}} = 39.6$ Hz, P–Si–H), 71.7 (d, $J_{\text{PP}} = 39.6$ Hz, P–Si $^+$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30°C , Ph–F/Tol- d_8): $\delta = 19.3$ (d, $J_{\text{SiP}} = 5.3$ Hz, SiMe $_2$), 11.6 (d, $J_{\text{SiP}} = 5.1$ Hz, SiMe $_2$), -18.5 (t, $J_{\text{SiP}} = 12.6$ Hz, P–Si–H), -22.5 (dd, $J_{\text{SiP}} = 22.3$ and 227.3 Hz, P–Si $^+$).

Compound 3a: (Different style from that used for Compound 3b)

3a·B(C $_6$ F $_5$) $_4$: To a mixture of **1-Cl** (0.32 g, 0.56 mmol) and dimethylsulfide (0.52 g, 8.45 mmol) in fluorobenzene (3 mL) was added KB(C $_6$ F $_5$) $_4$ (0.65 g, 0.91 mmol) at room temperature. After 3 h, the solution was filtered and all volatiles were removed under vacuum to obtain **3a·B(C $_6$ F $_5$) $_4$** as yellow powder (0.46 g, Yield: 65 %).

3a·B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$: To a mixture of chlorosilylene **1-Cl** (0.25 g, 0.45 mmol) and dimethylsulfide (0.42 g, 6.80 mmol) in toluene (3 mL) was added Li(Et $_2$ O) $_3$ B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$ (0.58 g, 0.45 mmol) at room temperature. After 12 h without stirring of solution, **3a·B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$** was obtained as yellow crystals (0.49 g, Yield: 67 %). Crystals suitable for X-ray diffraction were obtained from saturated toluene solution at ambient temperature.

3a·B[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$: In a Schlenk tube, **1-Cl** (500 mg, 0.89 mmol, 1.06 equiv) and NaB[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$ (740 mg, 0.84 mmol, 1 equiv) were dissolved in 3 mL of fluorobenzene. To this mixture, SMe $_2$ (0.7 mL, 9.55 mmol, 11 equiv.) was added at ambient temperature and keep stirring this solution at this temperature for 2 h. The precipitates were removed by filtration. Addition of pentane (ca. 20 mL) at room temperature leads to crystallization of **3a**, giving the corresponding **3a·B[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$** as yellow crystals (930 mg, 77 %). Mp. 125–126 °C (decomp.). ^1H NMR (300 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 0.20$ (s, 3H, SiCH $_3$), 0.34 (s, 3H, SiCH $_3$), 1.00 (d, $J_{\text{HH}} = 6.8$ Hz, 6H, CH $_3$ $_{\text{IPr}}$), 1.03 (s, 9H, CH $_3$ $_{\text{tBu}}$), 1.08 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.13 (overlapped, 1H, CH $_2$ $_{\text{Norb}}$), 1.13 (s, 9H, CH $_3$ $_{\text{tBu}}$), 1.27 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.40 (overlapped, 4H, CH $_2$ $_{\text{Norb}}$), 1.41 (br s, 6H, SCH $_3$), 2.28 (s, 1H, CH $_{\text{bridgehead}}$), 2.67 (sept, $J_{\text{HH}} = 6.6$ Hz, 1H, CH $_{\text{IPr}}$), 2.98 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH $_{\text{IPr}}$), 3.02 (s, 1H, CH $_{\text{bridgehead}}$), 7.06–7.12 (m, 1H, CH $_{\text{Ar}}$), 7.63 (s, 4H, P–CH $_{\text{BAr}}$), 8.31 (s, 8H, o-CH $_{\text{BAr}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 3.5$ (d, $J_{\text{PC}} = 2.1$ Hz, SiCH $_3$), 4.9 (d, $J_{\text{PC}} = 2.6$ Hz, SiCH $_3$), 20.1 (detected by ^1H - ^{13}C HSQC, SCH $_3$), 23.5 (CH $_3$ $_{\text{IPr}}$), 24.4 (CH $_3$ $_{\text{IPr}}$), 24.7 (CH $_3$ $_{\text{IPr}}$), 25.3 (CH $_2$ $_{\text{Norb}}$), 25.4 (CH $_3$ $_{\text{IPr}}$), 27.7 (CH $_{\text{IPr}}$), 28.0 (CH $_2$ $_{\text{Norb}}$), 29.3 (CH $_{\text{IPr}}$), 32.3 (d, $J_{\text{PC}} = 5.3$ Hz, CH $_3$ $_{\text{tBu}}$), 32.8 (d, $J_{\text{PC}} = 3.4$ Hz, CH $_3$ $_{\text{tBu}}$), 42.1 (d, $J_{\text{PC}} = 5.1$ Hz, CH $_{\text{bridgehead}}$), 43.9 (d, $J_{\text{PC}} = 12.6$ Hz, CH $_{\text{bridgehead}}$), 47.4 (d, $J_{\text{PC}} = 4.1$ Hz, CH $_2$ $_{\text{Norb}}$), 52.0 (C $_{\text{t-Bu}}$), 52.6 (C $_{\text{t-Bu}}$), 103.8 (d, $J_{\text{PC}} = 39.0$ Hz, P–C=C–N), 118.0 (br sept, $J_{\text{CF}} = 4.2$ Hz, P–CH $_{\text{BAr}}$), 125.0 (CH $_{\text{Ar}}$), 125.3 (q, $J_{\text{CF}} = 272.6$ Hz, CF $_3$), 126.0 (CH $_{\text{Ar}}$), 129.2 (CH $_{\text{Ar}}$), 130.0 (qq, $J_{\text{CF}} = 31.5$ Hz, $J_{\text{CF}} = 3.1$ Hz, m-CH $_{\text{BAr}}$), 134.2 (d, $J_{\text{PC}} = 4.9$ Hz, N-CH $_{\text{Ar}}$), 135.4 (o-CH $_{\text{BAr}}$), 146.1 (iPr-CH $_{\text{Ar}}$), 146.3 (iPr-CH $_{\text{Ar}}$), 162.8 (q, $J_{\text{CB}} = 49.8$ Hz, B–CH $_{\text{Ar}}$), 185.3 (d, $J_{\text{PC}} = 36.7$ Hz, P–C=C–N). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 67.0$ (s, Si-satellite: $J_{\text{SiP}} = 167.0$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = -15.6$ (d, $J_{\text{SiP}} = 167.0$ Hz, Si-SMe $_2$), 17.4 (d, $J_{\text{SiP}} = 4.6$ Hz, SiCH $_3$). $^{11}\text{B}\{^1\text{H}\}$ NMR (500 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = -6.0$ (BAr $_4$). $^{19}\text{F}\{^1\text{H}\}$ NMR (372.5 MHz, Ph–F/C $_6$ D $_6$): $\delta = -63.4$ (CF $_3$).

Compound 3b: 3b·B(C $_6$ F $_5$) $_4$: To a mixture of **1-Cl** (0.37 g, 0.67 mmol) and trimethylphosphine (0.34 mL, 3.35 mmol) in fluorobenzene (10 mL) was added KB(C $_6$ F $_5$) $_4$ (0.49 g, 0.67 mmol) at room temperature. After 30 min, the solution was filtered and all volatiles were removed under vacuum. To obtain **3b·B(C $_6$ F $_5$) $_4$** as yellow powder (0.68 g, Yield: 80 %).

3b·B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$: To a mixture of **1-Cl** (28 mg, 0.05 mmol) and trimethylphosphine (25 mL, 0.05 mmol) in toluene (0.5 mL) was

added Li(Et $_2$ O) $_3$ B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$ (65 mg, 0.45 mmol) at room temperature. After 12 h without stirring of solution, **3b·B(C $_6$ F $_4$ SiMe $_2$ t Bu) $_4$** was obtained as yellow crystals. The crystals suitable for X-ray diffraction were obtained from saturated toluene solution at ambient temperature.

3b·B[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$: In a Schlenk tube, **1-Cl** (670 mg, 1.19 mmol, 1.1 equiv) and NaB[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$ (940 mg, 1.06 mmol, 1 equiv) were dissolved in 7 mL of fluorobenzene. To this mixture, PMe $_3$ solution in toluene (1.0 M, 3.0 mL, 3.00 mmol, 2.8 equiv.) was added at ambient temperature and keep stirring this solution at this temperature for 1 h. The precipitates were removed by filtration. Addition of excess pentane (ca. 20 mL) at room temperature leads to crystallization of **3b**, giving the corresponding **3b·B[3,5-(CF $_3$) $_2$ C $_6$ H $_3$] $_4$** as yellow crystals (1.16 mg, 75 %). Mp: 172–174 °C (decomp.). (Major isomer, 85 %): ^1H NMR (300 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 0.24$ (s, 3H, SiCH $_3$), 0.37 (s, 3H, SiCH $_3$), 0.95 (d, $J_{\text{HP}} = 10.4$ Hz, 9H, P–CH $_3$), 0.97 (d, $J_{\text{HH}} = 6.6$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.04 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.07 (d, $J_{\text{HH}} = 6.6$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.09 (s, 9H, CH $_3$ $_{\text{tBu}}$), 1.13 (overlapped, 1H, CH $_2$ $_{\text{Norb}}$), 1.19 (s, 9H, CH $_3$ $_{\text{tBu}}$), 1.25 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.46 (m, 4H, CH $_2$ $_{\text{Norb}}$), 1.60 (m, 1H, CH $_2$ $_{\text{Norb}}$), 2.28 (m, 1H, CH $_{\text{bridgehead}}$), 2.68 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH $_{\text{IPr}}$), 2.87 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH $_{\text{IPr}}$), 3.10 (s, 1H, CH $_{\text{bridgehead}}$), 7.19–7.24 (m, 3H, CH $_{\text{Ar}}$), 7.62 (s, 4H, P–CH $_{\text{BAr}}$), 8.29 (s, 8H, o-CH $_{\text{BAr}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 3.6$ (d, $J_{\text{PC}} = 1.5$ Hz, SiCH $_3$), 5.1 (d, $J_{\text{PC}} = 1.6$ Hz, SiCH $_3$), 11.7 (dd, $J_{\text{PC}} = 30.8$ and 7.0 Hz, PCH $_3$), 23.9 (CH $_3$ $_{\text{IPr}}$), 24.1 (CH $_3$ $_{\text{IPr}}$), 25.1 (CH $_3$ $_{\text{IPr}}$), 25.4 (CH $_2$ $_{\text{Norb}}$), 26.5 (d, $J_{\text{PC}} = 1.7$ Hz, CH $_3$ $_{\text{IPr}}$), 27.9 (CH $_{\text{IPr}}$), 28.0 (CH $_2$ $_{\text{Norb}}$), 29.2 (CH $_{\text{IPr}}$), 32.3 (d, $J_{\text{PC}} = 6.2$ Hz, CH $_3$ $_{\text{tBu}}$), 32.8 (t, $J_{\text{PC}} = 2.7$ Hz, CH $_3$ $_{\text{tBu}}$), 41.9 (d, $J_{\text{PC}} = 4.0$ Hz, CH $_{\text{bridgehead}}$), 44.1 (d, $J_{\text{PC}} = 11.2$ Hz, CH $_{\text{bridgehead}}$), 47.5 (dd, $J_{\text{CP}} = 3.2$ and 2.1 Hz, CH $_2$ $_{\text{Norb}}$), 52.2 (C $_{\text{t-Bu}}$), 52.8 (C $_{\text{t-Bu}}$), 104.7 (d, $J_{\text{PC}} = 48.8$ Hz, P–C=C–N), 118.0 (br sept, $J_{\text{CF}} = 3.8$ Hz, o-CH $_{\text{BAr}}$), 124.4 (CH $_{\text{Ar}}$), 125.6 (d, $J_{\text{CF}} = 272.6$ Hz, CF $_3$), 125.8 (CH $_{\text{Ar}}$), 129.1 (CH $_{\text{Ar}}$), 129.9 (qq, $J_{\text{CB}} = 2.7$ Hz, $J_{\text{CF}} = 31.3$ Hz, m-CH $_{\text{BAr}}$), 135.4 (o-CH $_{\text{BAr}}$), 135.5 (overlapped, N-CH $_{\text{Ar}}$), 145.8 (iPr-CH $_{\text{Ar}}$), 146.7 (iPr-CH $_{\text{Ar}}$), 162.8 (q, $J_{\text{CB}} = 49.8$ Hz, B-CH $_{\text{Ar}}$), 181.1 (dd, $J_{\text{PC}} = 30.6$ and 6.9 Hz, P–C=C–N). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 64.3$ (d, $J_{\text{PP}} = 19.0$ Hz, Si-satellite: $J_{\text{SiP}} = 171.6$ Hz, PN), -28.8 (d, $J_{\text{PP}} = 19.1$ Hz, Si-satellite: $J_{\text{SiP}} = 224.0$ Hz, PMe $_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, CDCl $_3$, 25 °C): $\delta = -44.6$ (dd, $J_{\text{SiP}} = 171.6$ Hz, $J_{\text{SiP}} = 224.0$ Hz, P–Si–P), 13.3 (d, $J_{\text{SiP}} = 2.0$ Hz, SiCH $_3$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = -6.0$. ^{19}F NMR (470 MHz, Ph–F/C $_6$ D $_6$): $\delta = -62.3$ (CF $_3$). (Minor isomer, 15 %): ^1H NMR (300 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 0.23$ (s, 3H, SiCH $_3$), 0.35 (s, 3H, SiCH $_3$), 2.15 (m, 1H, CH $_{\text{bridgehead}}$), 2.55 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH $_{\text{IPr}}$), 3.01 (s, 1H, CH $_{\text{bridgehead}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = 3.4$ (d, $J_{\text{PC}} = 1.6$ Hz, SiCH $_3$), 5.5 (d, $J_{\text{PC}} = 1.6$ Hz, SiCH $_3$), 11.7 (dd, $J_{\text{PC}} = 31.3$ and 7.2 Hz, PCH $_3$), 23.7 (CH $_3$ $_{\text{IPr}}$), 23.8 (CH $_3$ $_{\text{IPr}}$), 25.6 (CH $_2$), 26.0 (CH $_3$ $_{\text{IPr}}$), 26.3 (CH $_3$ $_{\text{IPr}}$), 27.6 (CH $_{\text{IPr}}$), 29.1 (CH $_{\text{IPr}}$), 31.9 (d, $J_{\text{PC}} = 6.7$ Hz, CH $_3$ $_{\text{tBu}}$), 32.7 (t, $J_{\text{PC}} = 2.6$ Hz, CH $_3$ $_{\text{tBu}}$), 41.3 (d, $J_{\text{PC}} = 1.8$ Hz, CH $_{\text{bridgehead}}$), 43.5 (d, $J_{\text{PC}} = 12.8$ Hz, CH $_{\text{bridgehead}}$), 51.0 (d, $J_{\text{CP}} = 5.9$ Hz, CH $_2$ $_{\text{Norb}}$), 51.9 (C $_{\text{t-Bu}}$), 106.1 (d, $J_{\text{PC}} = 49.8$ Hz, P–C=C–N), 125.7 (CH $_{\text{Ar}}$), 128.3 (CH $_{\text{Ar}}$), 146.0 (iPr-CH $_{\text{Ar}}$), 147.3 (iPr-CH $_{\text{Ar}}$), 183.4 (dd, $J_{\text{PC}} = 30.5$ and 8.5 Hz, P–C=C–N). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, Ph–F/C $_6$ D $_6$, 25 °C): 61.9 (d, $J_{\text{PP}} = 23.1$ Hz, Si-satellite: $J_{\text{SiP}} = 162.5$ Hz, PN), -28.7 (d, $J_{\text{PP}} = 19.1$ Hz, Si-satellite: $J_{\text{SiP}} = 223.5$ Hz, PMe $_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59 MHz, Ph–F/C $_6$ D $_6$, 25 °C): $\delta = -29.6$ (dd, $J_{\text{SiP}} = 163.0$ Hz, $J_{\text{SiP}} = 224.4$ Hz, P–Si–P), 13.8 (d, $J_{\text{SiP}} = 2.1$ Hz, SiCH $_3$).

Compound 3c: To a mixture of **1-Cl** (0.89 g, 1.58 mmol) and DMAP (0.25 g, 2.05 mmol) in THF (10 mL), NaBPh $_4$ (0.54 g, 1.58 mmol) was added at room temperature. After 2.5 h, the solution was filtered and all volatiles were removed under vacuum. The residue was washed with pentane to obtain **3c** as yellow powder (1.25 g, Yield: 82 %). Crystals suitable for X-ray diffraction analysis were obtained from a solution in THF/Et $_2$ O at room temperature. Mp.: 111 °C. ^1H NMR (500 MHz, THF- d_8 , 25 °C): $\delta = 0.63$ (s, 3H, SiCH $_3$), 0.64 (s, 3H, SiCH $_3$), 0.88 (m, 3H, CH $_3$ $_{\text{IPr}}$), 1.10 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.15 (s, 9H, CH $_3$ $_{\text{tBu}}$), 1.19 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH $_3$ $_{\text{IPr}}$), 1.32 (m, CH $_3$ $_{\text{IPr}}$), 1.32 (m,

2H, CH_{2Norb}), 1.43 (m, 1H, CH_{2Norb}), 1.46 (s, 9H, CH_{3tBu}), 1.62 (m, 1H, CH_{2Norb}), 1.63 (m, 1H, CH_{2Norb}), 1.82 (m, 1H, CH_{2Norb}), 2.52 (s, 6H, NCH₃), 2.64 (s, 1H, CH_{bridgehead}), 2.99 (sept, J_{HH} = 6.5 Hz, 1H, CH_{ipr}), 3.35 (m, 1H, CH_{ipr}), 3.35 (m, 1H, CH_{bridgehead}), 6.38 (t, J_{HH} = 6.4 Hz, 2H, CH_{Ar}), 6.64 (t, J_{HH} = 7.2 Hz, 4H, CH_{Ar}), 6.79 (t, J_{HH} = 7.4 Hz, 8H, CH_{Ar}), 7.21 (m, 1H, CH_{Ar}), 7.27 (m, 8H, CH_{Ar}), 7.33 (m, 2H, CH_{Ar}), 7.36 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (75 MHz, THF-d₈, 25 °C): δ = 4.7 (d, J_{PC} = 2.3 Hz, SiCH₃), 5.8 (d, J_{PC} = 2.5 Hz, SiCH₃), 24.2 (CH_{3ipr}), 25.2 (CH_{3ipr}), 25.4 (CH_{3ipr}), 26.6 (CH₂), 26.7 (CH_{3ipr}), 28.9 (CH_{ipr}), 29.0 (d, J_{PC} = 1.7 Hz, CH_{2Norb}), 30.2 (CH_{ipr}), 33.0 (d, J_{PC} = 3.5 Hz, CH_{3tBu}), 33.8 (CH_{3tBu}), 39.7 (NCH₃), 42.6 (d, J_{PC} = 5.9 Hz, CH_{bridgehead}), 44.8 (d, J_{PC} = 12.0 Hz, CH_{bridgehead}), 47.2 (d, J_{PC} = 6.4 Hz, CH_{2Norb}), 52.6 (C_{t-Bu}), 53.5 (C_{t-Bu}), 103.2 (d, J_{PC} = 43.5 Hz, P—C—N), 109.2 (CH_{Ar}), 122.0 (q, CH_{Ar}), 125.8 (CH_{Ar}), 125.9 (q, CH_{Ar}), 126.4 (CH_{Ar}), 129.3 (CH_{Ar}), 137.3 (q, CH_{Ar}), 137.7 (d, J_{PC} = 3.4 Hz, N—C_{Ar}), 143.7 (iPr—C_{Ar}), 147.3 (iPr—C_{Ar}), 147.5 (C_{Ar}), 156.6 (C_{Ar}), 165.4 (q, C_{Ar}), 180.3 (d, J_{PC} = 33.5 Hz, P—C—N). ³¹P{¹H} NMR (121 MHz, THF-d₈, 25 °C): δ = 64.7 (s, Si-satellite: J_{SiP} = 178.4 Hz). ²⁹Si{¹H} NMR (99 MHz, THF-d₈, 25 °C): δ = -14.5 (d, J_{SiP} = 178.4 Hz, Si-DMAP), 13.7 (d, J_{SiP} = 3.1 Hz, SiCH₃). ¹¹B{¹H} NMR (160 MHz, THF-d₈, 25 °C): δ = -6.5.

Compound 3d: To a mixture of 1-Cl (1.05 g, 1.86 mmol) and NHC (0.30 g, 2.42 mmol) in THF (10 mL) was added NaBPh₄ (0.64 g, 1.86 mmol) at room temperature. After 15 minutes, the solution was filtered and all volatiles were removed under vacuum. The residue was washed with pentane to obtain **3d** as orange powder (1.31 g, Yield: 73 %). Crystals suitable for X-ray diffraction analysis were obtained from a solution in THF/Et₂O at -30 °C. Mp: 215 °C. ¹H NMR (500 MHz, THF-d₈, 25 °C): δ = 0.52 (s, 3H, SiCH₃), 0.66 (s, 3H, SiCH₃), 0.67 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.07 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.19 (d, J_{HH} = 6.7 Hz, 3H, CH_{3ipr}), 1.21 (s, 9H, CH_{3tBu}), 1.38 (d, J_{HH} = 6.7 Hz, 3H, CH_{3ipr}), 1.43 (d, J_{HH} = 8.6 Hz, 1H, CH_{2Norb}), 1.47 (s, 9H, CH_{3tBu}), 1.64 (m, 1H, CH_{2Norb}), 1.65 (m, 1H, CH_{2Norb}), 1.69 (m, 2H, CH_{2Norb}), 1.73 (s, 6H, C=C(NH)C), 1.83 (m, 1H, CH_{2Norb}), 2.63 (s, 1H, CH_{bridgehead}), 2.88 (sept, J_{HH} = 7.1 Hz, 1H, CH_{ipr}), 3.00 (s, 6H, C=C(CH₃)), 3.24 (sept, J_{HH} = 7.1 Hz, 1H, CH_{ipr}), 3.38 (s, 1H, CH_{bridgehead}), 6.65 (t, J_{HH} = 7.2 Hz, 4H, CH_{Ar}), 6.80 (t, J_{HH} = 7.4 Hz, 8H, CH_{Ar}), 7.19 (dd, J_{HH} = 7.4 Hz, 1.8 Hz, 1H, CH_{Ar}), 7.25 (m, 8H, CH_{Ar}), 7.29 (m, 8H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, THF-d₈, 25 °C): δ = 3.8 (d, J_{PC} = 2.8 Hz, SiCH₃), 5.9 (d, J_{PC} = 3.0 Hz, SiCH₃), 8.8 (C=C—CH₂NHC), 20.8 (CH_{3ipr}), 24.9 (CH_{3ipr}), 25.5 (CH_{3ipr}), 26.1 (d, J_{PC} = 2.2 Hz, CH_{3ipr}), 26.5 (d, J_{PC} = 2.2 Hz, CH_{2Norb}), 28.7 (d, J_{PC} = 1.9 Hz, CH_{2Norb}), 28.8 (CH_{ipr}), 29.7 (CH_{ipr}), 35.2 (d, J_{PC} = 4.0 Hz, N—CH₃NHC), 32.5 (d, J_{PC} = 5.6 Hz, CH_{3tBu}), 34.0 (d, J_{PC} = 2.8 Hz, CH_{3tBu}), 43.4 (d, J_{PC} = 4.4 Hz, CH_{bridgehead}), 44.8 (d, J_{PC} = 11.1 Hz, CH_{bridgehead}), 48.3 (d, J_{PC} = 3.6 Hz, CH_{2Norb}), 52.8 (d, J_{PC} = 1.3 Hz, C_{t-Bu}), 53.9 (C_{t-Bu}), 102.8 (d, J_{PC} = 48.0 Hz, P—C—N), 121.9 (CH_{Ar}), 125.6 (CH_{Ar}), 125.9 (q, CH_{Ar}), 126.4 (s, CH_{Ar}), 129.7 (CH_{Ar}), 130.1 (C=C(NH)C), 137.3 (q, CH_{Ar}), 139.7 (d, J_{PC} = 1.7 Hz, N—C_{Ar}), 147.5 (iPr—C_{Ar}), 147.8 (iPr—C_{Ar}), 157.1 (d, J_{PC} = 6.7 Hz, C_{carbene}), 165.3 (q, C_{Ar}), 178.1 (d, J_{PC} = 32.0 Hz, P—C—N). ³¹P{¹H} NMR (162 MHz, THF-d₈, 25 °C): δ = 67.6 (s, Si-satellite: J_{SiP} = 196.6 Hz). ²⁹Si{¹H} NMR (79 MHz, THF-d₈, 25 °C): δ = -26.8 (d, J_{SiP} = 196.5 Hz, Si—NHC), 12.0 (d, J_{SiP} = 3.4 Hz, SiCH₃). ¹¹B{¹H} NMR (96 MHz, THF-d₈, 25 °C): δ = -6.5.

Compound 5: To a mixture of **3a** (0.29 g, 0.24 mmol) in fluorobenzene (2 mL) was added 1,3-dimethyl-2,3-dimethylbutadiene (2.7 μ L, 0.23 mmol) at room temperature. After 20 minutes, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **5** as orange powder (0.24 g, Yield: 81 %). Crystals suitable for X-ray diffraction analysis were obtained from a solution in CDCl₃/pentane at RT. Mp.: 171 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 0.56 (s, 3H, SiCH₃), 0.75 (s, 3H, SiCH₃), 1.16 (d, J_{HH} = 6.7 Hz, 6H, CH_{3ipr}), 1.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.28 (d, J_{HH} = 6.7 Hz, 3H, CH_{3ipr}), 1.35 (overlapped, 1H, CH₂), 1.35 (s, 9H, CH_{3tBu}), 1.37 (s, 9H, CH_{3tBu}), 1.55 (m, 1H, CH_{2Norb}), 1.60 (s, 3H, H₃CC=CCH₃), 1.69 (s, 3H, H₃CC=CCH₃), 1.73 (m, 2H, CH_{2Norb}), 1.92 (m, 4H, CH_{2Norb} and Si—CH₂), 2.06 (brs, 2H, Si—CH₂), 2.71 (brs, 1H, CH_{bridgehead}), 2.80 (sept, J_{HH} = 6.8 Hz, 1H, CH_{ipr}), 2.95 (sept, J_{HH} = 6.8 Hz,

1H, CH_{ipr}), 3.37 (brs, 1H, CH_{bridgehead}), 7.22 (d, 1H, J_{HH} = 7.8 Hz, CH_{Ar}), 7.23 (d, 1H, J_{HH} = 7.8 Hz, CH_{Ar}), 7.36 (t, 1H, J_{HH} = 7.8 Hz, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ = 4.1 (d, J_{PC} = 1.9 Hz, SiCH₃), 5.6 (SiCH₃), 18.4 (H₃CC=CCH₃), 18.5 (H₃CC=CCH₃), 22.8 (d, J_{PC} = 11.5 Hz, Si—CH₂), 23.9 (d, J_{PC} = 14.0 Hz, Si—CH₂), 24.4 (CH_{3ipr}), 24.6 (CH_{3ipr}), 25.2 (CH_{3ipr}), 25.2 (d, J_{PC} = 1.3 Hz, CH_{2Norb}), 25.6 (CH_{3ipr}), 27.8 (CH_{2Norb}), 28.1 (CH_{ipr}), 28.2 (CH_{ipr}), 32.1 (d, J_{PC} = 5.8 Hz, CH_{3tBu}), 32.5 (d, J_{PC} = 5.7 Hz, CH_{3tBu}), 41.1 (CH_{bridgehead}), 44.1 (d, J_{PC} = 10.2 Hz, CH_{bridgehead}), 48.3 (d, J_{PC} = 6.1 Hz, CH_{2Norb}), 53.0 (brs, 2 x C_{t-Bu}), 98.4 (d, J_{PC} = 68.5 Hz, P—C—N), 125.4 (2 x CH_{Ar}), 129.4 (d, J_{PC} = 4.0 Hz, H₃CC=CCH₃), 129.7 (CH_{Ar}), 130.0 (d, J_{PC} = 3.7 Hz, H₃CC=CCH₃), 132.0 (d, J_{PC} = 3.3 Hz, N—C_{Ar}), 136.4 (d, J_{CF} = 244.5 Hz, C_{Ar}), 138.3 (d, J_{CF} = 244.5 Hz, C_{Ar}), 146.3 (iPr—C_{Ar}), 146.7 (iPr—C_{Ar}), 148.3 (d, J_{CF} = 242.4 Hz, C_{Ar}), 192.2 (d, J_{PC} = 25.5 Hz, P—C—N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): δ = 37.6 (s, Si-satellite: J_{SiP} = 125.6 Hz). ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): δ = 11.1 (d, J_{SiP} = 125.6 Hz, SiP), 21.6 (d, J_{SiP} = 2.8 Hz, SiCH₃). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 25 °C): δ = -16.6. ¹⁹F NMR (470 MHz, CDCl₃, 25 °C): δ = -132.5 (m, B(C₆F₅)₄), -163.4 (t, J_{FF} = 20.5 Hz, B(C₆F₅)₄), -167.0 (t, J_{FF} = 19.6 Hz, B(C₆F₅)₄).

Compound 6-A: To a mixture of **3a** (0.29 g, 0.23 mmol) in fluorobenzene (2 mL) was added diphenylacetylene (4.2 mg, 0.23 mmol) at room temperature. After 1 h, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **6-A** as yellow powder (0.26 g, Yield: 80 %). Crystals suitable for X-ray diffraction analysis were obtained from a solution in CDCl₃/pentane at room temperature. Mp.: 221 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 0.57 (s, 3H, SiCH₃), 0.74 (s, 3H, SiCH₃), 0.93 (d, J_{HH} = 6.7 Hz, 3H, CH_{3ipr}), 0.95 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.21 (d, 6H, J_{HH} = 6.8 Hz, CH_{3ipr}), 1.46 (overlapped, 1H, CH₂), 1.46 (s, 18H, CH_{3tBu}), 1.59 (m, 1H, CH_{2Norb}), 1.76 (m, 2H, CH_{2Norb}), 1.98 (m, 2H, CH_{2Norb}), 2.86 (brs, 1H, CH_{bridgehead}), 3.07 (sept, J_{HH} = 6.8 Hz, 1H, CH_{ipr}), 3.17 (sept, J_{HH} = 6.8 Hz, 1H, CH_{ipr}), 3.46 (brs, 1H, CH_{bridgehead}), 7.14 (m, 4H, CH_{Ar}), 7.35 (m, 7H, CH_{Ar}), 7.47 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ = 4.2 (d, J_{PC} = 1.6 Hz, SiCH₃), 5.0 (SiCH₃), 24.2 (CH_{3ipr}), 24.5 (CH_{3ipr}), 24.7 (CH_{3ipr}), 25.2 (d, J_{PC} = 1.6 Hz, CH_{2Norb}), 25.2 (CH_{3ipr}), 28.0 (CH_{2Norb}), 28.6 (CH_{ipr}), 29.0 (CH_{ipr}), 32.2 (d, J_{PC} = 6.5 Hz, CH_{3tBu}), 32.5 (d, J_{PC} = 6.2 Hz, CH_{3tBu}), 41.1 (CH_{bridgehead}), 45.8 (d, J_{PC} = 8.9 Hz, CH_{bridgehead}), 47.5 (d, J_{PC} = 6.9 Hz, CH_{2Norb}), 53.2 (2 x C_{t-Bu}), 97.6 (d, J_{PC} = 78.2 Hz, P—C—N), 125.0 (2 x CH_{Ar}), 127.8 (CH_{Ar}), 127.9 (CH_{Ar}), 128.4 (CH_{Ar}), 128.5 (CH_{Ar}), 129.1 (2 x CH_{Ar}), 129.7 (d, J_{PC} = 1.4 Hz, CH_{Ar}), 129.7 (CH_{Ar}), 129.8 (CH_{Ar}), 130.0 (d, J_{PC} = 2.8 Hz, C_{Ar}), 130.8 (CH_{Ar}), 131.3 (d, J_{PC} = 2.4 Hz, C_{Ar}), 131.7 (CH_{Ar}), 131.8 (d, J_{PC} = 2.6 Hz, C_{Ar}), 136.4 (d, J_{CF} = 244.2 Hz, C_{Ar}), 139.3 (d, J_{CF} = 244.2 Hz, C_{Ar}), 146.3 (iPr—C_{Ar}), 146.5 (C_{Ar}), 148.3 (d, J_{CF} = 241.2 Hz, C_{Ar}), 152.4 (d, J_{PC} = 5.0 Hz, PhC=CPh), 154.4 (d, J_{PC} = 2.4 Hz, PhC=CPh), 193.3 (d, J_{PC} = 20.7 Hz, P—C—N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): δ = 23.9 (s, Si-satellite: J_{SiP} = 186.5 Hz). ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): δ = -96.4 (d, J_{SiP} = 186.6 Hz, SiP), 21.4 (d, J_{SiP} = 2.4 Hz, SiCH₃). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 25 °C): δ = -16.6. ¹⁹F NMR (470 MHz, CDCl₃, 25 °C): -132.5 (m, B(C₆F₅)₄), -163.3 (t, J_{FF} = 20.5 Hz, B(C₆F₅)₄), -166.9 (t, J_{FF} = 19.5 Hz, B(C₆F₅)₄).

Compound 6-B: To a mixture of **3a** (1.01 g, 0.80 mmol) in fluorobenzene (4 mL) was added bis(trimethylsilyl)acetylene (0.18 mL, 0.80 mmol) at room temperature. After 12 h, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **6-B** as yellow powder (0.84 g, Yield: 76 %). Crystals suitable for X-ray diffraction analysis were obtained from a solution in CDCl₃/pentane at room temperature. Mp.: 183 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 0.14 (s, 9H, SiMe₃), 0.14 (s, 9H, C—SiMe₃), 0.34 (s, 9H, C—SiMe₃), 0.51 (s, 3H, SiCH₃), 0.73 (s, 3H, SiCH₃), 1.16 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.20 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.31 (d, J_{HH} = 6.8 Hz, 3H, CH_{3ipr}), 1.42 (m, 1H, CH_{2Norb}), 1.44 (d, J_{HH} = 1.2 Hz, 9H, CH_{3tBu}), 1.47 (d, J_{HH} = 1.2 Hz, 9H, CH_{3tBu}), 1.58 (m, 1H, CH_{2Norb}), 1.73 (m, 1H, CH_{2Norb}), 1.76 (m, 1H, CH_{2Norb}), 1.91 (m, 1H, CH_{2Norb}), 1.99 (m, 1H, CH_{2Norb}), 2.83 (m, 1H,

$\text{CH}_{\text{bridgehead}}$, 2.98 (m, 2H, CH_{IPr}), 3.43 (brs, 1H, $\text{CH}_{\text{bridgehead}}$), 7.19 (dd, $J_{\text{HH}}=1.6$ and 7.8 Hz, 1H, CH_{Ar}), 7.24 (dd, $J_{\text{HH}}=1.6$ and 7.8 Hz, 1H, CH_{Ar}), 7.34 (t, $J_{\text{HH}}=7.8$ Hz, 1H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C): $\delta=0.1$ ($\text{Si}(\text{CH}_3)_3$), 0.7 ($\text{Si}(\text{CH}_3)_3$), 4.0 (d, $J_{\text{PC}}=1.5$ Hz, SiCH_3), 4.8 (SiCH_3), 23.8 ($\text{CH}_{3\text{IPr}}$), 24.6 ($\text{CH}_{3\text{IPr}}$), 25.0 (d, $J_{\text{PC}}=1.2$ Hz, CH_2), 25.1 ($\text{CH}_{3\text{IPr}}$), 25.9 ($\text{CH}_{2\text{Norb}}$), 25.9 ($\text{CH}_{3\text{IPr}}$), 28.2 (CH_{IPr}), 28.3 (CH_{IPr}), 32.4 (d, $J_{\text{PC}}=6.4$ Hz, $\text{CH}_{3\text{IBu}}$), 32.5 (d, $J_{\text{PC}}=6.3$ Hz, $\text{CH}_{3\text{IBu}}$), 40.8 ($\text{CH}_{\text{bridgehead}}$), 46.0 (d, $J_{\text{PC}}=8.7$ Hz, $\text{CH}_{\text{bridgehead}}$), 47.3 (d, $J_{\text{PC}}=6.8$ Hz, $\text{CH}_{2\text{Norb}}$), 52.9 ($\text{C}_{\text{t-Bu}}$), 53.0 ($\text{C}_{\text{t-Bu}}$), 96.8 (d, $J_{\text{PC}}=79.8$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$), 124.6 (CH_{Ar}), 124.8 (CH_{Ar}), 129.3 (CH_{Ar}), 131.8 (d, $J_{\text{PC}}=2.2$ Hz, $\text{N}-\text{C}_{\text{Ar}}$), 136.2 (d, $J_{\text{CF}}=245.5$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 138.1 (d, $J_{\text{CF}}=245.5$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 145.7 (iPr- C_{Ar}), 145.9 (iPr- C_{Ar}), 148.2 (d, $J_{\text{CF}}=241.3$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 189.2 (d, $J_{\text{PC}}=8.0$ Hz, $\text{TMSC}=\text{CTMS}$), 189.7 (d, $J_{\text{PC}}=4.3$ Hz, $\text{TMSC}=\text{CTMS}$), 192.5 (d, $J_{\text{PC}}=20.5$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 25 °C): $\delta=33.6$ (s, Si-satellite: $J_{\text{SiP}}=215.8$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, $\text{Ph}-\text{F}/\text{C}_6\text{D}_6$, 25 °C): $\delta=-100.1$ (d, $J_{\text{SiP}}=216.1$ Hz, SiP), -7.5 (d, $J_{\text{SiP}}=2.6$ Hz, TMS), 19.4 (d, $J_{\text{SiP}}=1.7$ Hz, SiCH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 25 °C): $\delta=-16.1$. ^{19}F NMR (470 MHz, CDCl_3 , 25 °C): -132.2 (m, $\text{B}(\text{C}_6\text{F}_5)_4$), -163.3 (t, $J_{\text{FF}}=20.4$ Hz, $\text{B}(\text{C}_6\text{F}_5)_4$), -166.9 (t, $J_{\text{FF}}=19.2$ Hz, $\text{B}(\text{C}_6\text{F}_5)_4$).

Compound 6-C: To a mixture of **3a** (0.49 g, 0.39 mmol) in fluorobenzene (2.5 mL) was added dimesitylacetylene (0.10 g, 0.39 mmol) at room temperature. After 48 h, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **6-C** as yellow powder (0.33 g, Yield: 58%). Mp.: 126 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta=0.62$ (s, 3H, SiCH_3), 0.80 (s, 3H, SiCH_3), 0.78 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.10 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.22 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.24 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.28 (d, 9H, $\text{CH}_{3\text{IBu}}$), 1.49 (d, 9H, $\text{CH}_{3\text{IBu}}$), 1.60 (m, 1H, $\text{CH}_{2\text{Norb}}$), 1.63 (m, 1H, $\text{CH}_{2\text{Norb}}$), 1.78 (m, 2H, $\text{CH}_{2\text{Norb}}$), 1.80 (s, 6H, CH_3Mes), 2.05 (m, 2H, $\text{CH}_{2\text{Norb}}$), 2.07 (s, 6H, CH_3Mes), 2.22 (s, 3H, CH_3Mes), 2.23 (s, 3H, CH_3Mes), 3.00 (m, 1H, $\text{CH}_{\text{bridgehead}}$), 3.08 (m, 2H, CH_{IPr}), 3.50 (brs, 1H, $\text{CH}_{\text{bridgehead}}$), 6.76 (m, 1H, CH_{Ar}), 6.80 (m, 1H, CH_{Ar}), 7.15 (dd, $J_{\text{HH}}=1.6$ and 7.7 Hz, 1H, CH_{Ar}), 7.29 (m, 1H, CH_{Ar}), 7.38 (t, $J_{\text{HH}}=7.7$ Hz, 1H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C): $\delta=4.0$ (d, $J_{\text{PC}}=2.3$ Hz, SiCH_3), 5.3 (SiCH_3), 20.8 (CH_3), 20.9 (CH_3), 21.2 (2 x CH_3), 22.1 (2 x CH_3), 22.3 ($\text{CH}_{3\text{IPr}}$), 24.1 ($\text{CH}_{3\text{IPr}}$), 26.0 (brs, CH_2), 26.0 ($\text{CH}_{3\text{IPr}}$), 26.7 ($\text{CH}_{3\text{IPr}}$), 27.6 ($\text{CH}_{2\text{Norb}}$), 28.2 (CH_{IPr}), 28.3 (CH_{IPr}), 31.6 (d, $J_{\text{PC}}=6.1$ Hz, $\text{CH}_{3\text{IBu}}$), 32.1 (d, $J_{\text{PC}}=6.3$ Hz, $\text{CH}_{3\text{IBu}}$), 41.8 ($\text{CH}_{\text{bridgehead}}$), 46.5 (d, $J_{\text{PC}}=8.6$ Hz, $\text{CH}_{\text{bridgehead}}$), 47.6 (d, $J_{\text{PC}}=6.1$ Hz, $\text{CH}_{2\text{Norb}}$), 53.2 ($\text{C}_{\text{t-Bu}}$), 53.3 ($\text{C}_{\text{t-Bu}}$), 97.9 (d, $J_{\text{PC}}=71.1$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$), 125.2 (CH_{Ar}), 125.4 (CH_{Ar}), 127.7 (brs, 2 x CH_{Ar}), 128.7 (d, $J_{\text{PC}}=3.4$ Hz, C_{Ar}), 128.8 (CH_{Ar}), 128.9 (CH_{Ar}), 129.7 (CH_{Ar}), 130.2 (d, $J_{\text{PC}}=2.6$ Hz, C_{Ar}), 132.0 (d, $J_{\text{PC}}=2.5$ Hz, C_{Ar}), 133.2 (d, $J_{\text{PC}}=0.8$ Hz, C_{Ar}), 134.1 (d, $J_{\text{PC}}=1.1$ Hz, C_{Ar}), 136.2 (d, $J_{\text{CF}}=245.0$ Hz, C_{Ar}), 137.4 (C_{Ar}), 138.2 (C_{Ar}), 138.2 (d, $J_{\text{CF}}=245.0$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 138.8 (C_{Ar}), 139.8 (C_{Ar}), 146.9 (C_{Ar}), 147.2 (C_{Ar}), 148.2 (d, $J_{\text{CF}}=242.8$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 158.7 (d, $J_{\text{PC}}=1.1$ Hz, $\text{MesC}=\text{CMes}$), 160.3 (d, $J_{\text{PC}}=7.9$ Hz, $\text{MesC}=\text{CMes}$), 193.2 (d, $J_{\text{PC}}=20.9$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3 , 25 °C): $\delta=27.6$ (s, Si-satellite: $J_{\text{SiP}}=174.2$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, $\text{Ph}-\text{F}/\text{C}_6\text{D}_6$, 25 °C): $\delta=-86.9$ (d, $J_{\text{SiP}}=174.2$ Hz, SiP), 21.7 (d, $J_{\text{SiP}}=2.8$ Hz, SiCH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 25 °C): $\delta=-16.6$. ^{19}F NMR (470 MHz, CDCl_3 , 25 °C): $\delta=-132.5$ (m, $\text{B}(\text{C}_6\text{F}_5)_4$), -163.3 (t, $J_{\text{FF}}=20.5$ Hz, $\text{B}(\text{C}_6\text{F}_5)_4$), -166.9 (t, $J_{\text{FF}}=19.6$ Hz, $\text{B}(\text{C}_6\text{F}_5)_4$).

Compound 7: In a pressure NMR tube, fluorobenzene/ C_6D_6 (0.4 + 0.1 mL) solution of **3b** (114 mg, 0.089 mmol) were exposed to a 3 bar of CO_2 at ambient temperature. This reaction was monitored by ^{31}P NMR and completed after 30 min. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from fluorobenzene solution. Due to the low solubility of **7** after crystallization, full characterization of **7** by NMR were not succeeded. (Major isomer, 82%): $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $\text{C}_6\text{D}_6/\text{Ph}-\text{F}$, 25 °C): $\delta=85.4$ (d, $J_{\text{PP}}=2.9$ Hz, $\text{N}-\text{Si}-\text{P}$), 20.0 (d, $J_{\text{PP}}=2.9$ Hz, $\text{P}=\text{O}$). (Minor isomer, 18%): $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $\text{C}_6\text{D}_6/\text{Ph}-\text{F}$, 25 °C): $\delta=85.7$ (s, $\text{N}-\text{Si}-\text{P}$), 19.7 (s, $\text{P}=\text{O}$).

Compound 8-A: In a J. Young NMR tube, to a solution of **3a** (100 mg, 0.069 mmol) in fluorobenzene (0.5 mL), diphenylphosphine (12 μL , 0.069 mmol) was added at ambient temperature. The color of solution changed from yellow to colorless within 1 min. Addition of excess pentane (ca. 1.5 mL) at room temperature leads to crystallization of **8-A**, giving the corresponding **8-A** as colorless crystals (102 mg, 92%). Mp: 172–175 °C (decomp.). (Major isomer, 90%): ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta=0.11$ (s, 3H, SiCH_3), 0.58 (s, 3H, SiCH_3), 0.64 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.11 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.28 (overlapped, 3H, $\text{CH}_{3\text{IPr}}$), 1.28 (s, 9H, $\text{CH}_{3\text{IBu}}$), 1.31 (s, 9H, $\text{CH}_{3\text{IBu}}$), 1.54 (d, $J_{\text{HH}}=6.7$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.59 (d, $J_{\text{HH}}=9.0$ Hz, 1H, $\text{CH}_{2\text{Norb}}$), 1.65 (m, 1H, $\text{CH}_{2\text{Norb}}$), 1.83 (d, $J_{\text{HH}}=9.0$ Hz, 1H, $\text{CH}_{2\text{Norb}}$), 1.91 (m, 3H, $\text{CH}_{2\text{Norb}}$), 2.73 (sept, $J_{\text{HH}}=6.8$ Hz, 1H, CH_{IPr}), 2.87 (m, 1H, $\text{CH}_{\text{bridgehead}}$), 3.19 (sept, $J_{\text{HH}}=6.7$ Hz, 1H, CH_{IPr}), 3.34 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 5.77 (dd, $J_{\text{HP}}=36.7$ and 3.8 Hz, Si-satellite : $J_{\text{HSi}}=233.6$ Hz, Si-H), 6.45 (dd, $J_{\text{HP}}=8.6$ Hz, $J_{\text{HH}}=7.9$ Hz, 2H, CH_{PPh}), 6.94 (t, $J_{\text{HH}}=7.0$ Hz, 2H, CH_{PPh}), 7.10–7.14 (m, 2H, CH_{Ar}), 7.37 (d, $J_{\text{HH}}=7.1$ Hz, 1H, CH_{Ar}), 7.47 (t, $J_{\text{HH}}=7.7$ Hz, 1H, CH_{PPh}), 7.52 (dd, $J_{\text{HH}}=14.7$ and 8.0 Hz, 3H, CH_{PPh}), 7.56 (s, 4H, $\text{P}-\text{CH}_{\text{BAr}}$), 7.68 (dd, $J_{\text{HP}}=7.0$ Hz, $J_{\text{HH}}=7.3$ Hz, 2H, CH_{PPh}), 7.76 (s, 8H, $\text{o}-\text{CH}_{\text{BAr}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C): $\delta=3.3$ (d, $J_{\text{CP}}=2.2$ Hz, SiCH_3), 5.8 (SiCH_3), 23.9 ($\text{CH}_{3\text{IPr}}$), 24.6 ($\text{CH}_{3\text{IPr}}$), 24.7 ($\text{CH}_{3\text{IPr}}$), 24.7 ($\text{CH}_{3\text{IPr}}$), 25.0 ($\text{CH}_{2\text{Norb}}$), 27.9 ($\text{CH}_{2\text{Norb}}$), 28.6 (CH_{IPr}), 28.7 (d, $J_{\text{CP}}=1.9$ Hz, CH_{IPr}), 32.4 (t, $J_{\text{CP}}=5.7$ Hz, $\text{CH}_{3\text{IBu}}$), 32.8 (d, $J_{\text{CP}}=5.7$ Hz, $\text{CH}_{3\text{IBu}}$), 41.7 ($\text{CH}_{\text{bridgehead}}$), 44.7 (d, $J_{\text{CP}}=10.4$ Hz, $\text{CH}_{\text{bridgehead}}$), 48.6 ($J_{\text{CP}}=5.0$ Hz, $\text{CH}_{2\text{Norb}}$), 52.7 ($\text{C}_{\text{t-Bu}}$), 53.4 ($\text{C}_{\text{t-Bu}}$), 100.5 (d, $J_{\text{CP}}=70.0$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$), 117.6 (br sept, $J_{\text{CF}}=3.8$ Hz, $\text{P}-\text{CH}_{\text{BAr}}$), 124.7 (q, $J_{\text{CF}}=272.5$ Hz, CF_3), 125.7 (CH_{Ar}), 125.9 (CH_{Ar}), 129.1 (CH_{Ar}), 129.1 (qq, $J_{\text{CF}}=31.6$ Hz, $J_{\text{CB}}=2.7$ Hz, $\text{m}-\text{CH}_{\text{BAr}}$), 129.4 (d, $J_{\text{CP}}=6.8$ Hz, CH_{PPh}), 130.2 (dd, $J_{\text{CP}}=20.7$ and 5.3 Hz, C_{PPh}), 130.3 (d, $J_{\text{CP}}=5.4$ Hz, CH_{PPh}), 131.7 (CH_{PPh}), 132.3 (d, $J_{\text{CP}}=18.3$ Hz, CH_{PPh}), 135.0 (d, $J_{\text{CP}}=2.2$ Hz, $\text{N}-\text{C}_{\text{Ar}}$), 135.0 ($\text{o}-\text{CH}_{\text{BAr}}$), 137.0 (d, $J_{\text{CP}}=21.1$ Hz, CH_{PPh}), 146.0 (iPr- C_{Ar}), 146.7 (iPr- C_{Ar}), 161.9 (q, $J_{\text{CB}}=49.8$ Hz, $\text{B}-\text{C}_{\text{Ar}}$), 191.4 (d, $J_{\text{CP}}=25.3$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 25 °C): $\delta=-74.2$ (d, $J_{\text{PP}}=11.5$ Hz, Si-satellite: $J_{\text{SiP}}=73.0$ Hz, PPh₂), 38.8 (d, $J_{\text{PP}}=11.6$ Hz, Si-satellite: $J_{\text{SiP}}=100.0$ Hz, $\text{C}=\text{C}-\text{P}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, CDCl_3 , 25 °C): $\delta=-18.7$ (dd, $J_{\text{SiP}}=72.6$ Hz, $J_{\text{SiP}}=100.6$ Hz, $\text{P}-\text{Si}-\text{P}$), 22.1 (d, $J_{\text{SiP}}=3.2$ Hz, SiCH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 25 °C): $\delta=-6.6$. ^{19}F NMR (470 MHz, CDCl_3 , 25 °C): $\delta=-62.4$ (CF_3). (Minor isomer, 10%): ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta=0.14$ (s, 3H, SiCH_3), 0.98 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.16 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.21 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.27 (s, 9H, $\text{CH}_{3\text{IBu}}$), 1.33 (d, $J_{\text{HH}}=7.0$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.77 (d, $J_{\text{HH}}=8.7$ Hz, 1H, $\text{CH}_{2\text{Norb}}$), 2.80 (m, 1H, $\text{CH}_{\text{bridgehead}}$), 5.75 (dd, $J_{\text{HP}}=36.1$ and 4.2 Hz, Si-H), 6.51 (dd, $J_{\text{HP}}=7.4$ Hz, $J_{\text{HH}}=7.9$ Hz, 2H, CH_{PPh}). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C): $\delta=3.3$ (d, $J_{\text{CP}}=3.4$ Hz, SiCH_3), 5.8 (SiCH_3), 24.2 ($\text{CH}_{3\text{IPr}}$), 24.3 ($\text{CH}_{3\text{IPr}}$), 24.3 ($\text{CH}_{3\text{IPr}}$), 24.4 ($\text{CH}_{3\text{IPr}}$), 27.7 ($\text{CH}_{2\text{Norb}}$), 28.3 (CH_{IPr}), 28.7 (CH_{IPr}), 32.2 (t, $J_{\text{CP}}=59.7$ Hz, $\text{CH}_{3\text{IBu}}$), 44.4 (d, $J_{\text{CP}}=10.9$ Hz, $\text{CH}_{\text{bridgehead}}$), 49.7 ($J_{\text{CP}}=7.4$ Hz, $\text{CH}_{2\text{Norb}}$), 52.8 ($\text{C}_{\text{t-Bu}}$), 53.5 ($\text{C}_{\text{t-Bu}}$), 102.5 (d, $J_{\text{CP}}=69.1$ Hz, $\text{P}-\text{C}=\text{C}-\text{N}$), 125.6 (CH_{Ar}), 125.7 (CH_{Ar}), 129.1 (CH_{Ar}), 129.3 (d, $J_{\text{CP}}=6.5$ Hz, CH_{PPh}), 131.1 (dd, $J_{\text{CP}}=19.4$ and 5.5 Hz, C_{PPh}), 131.7 (CH_{PPh}), 136.8 (d, $J_{\text{CP}}=20.9$ Hz, CH_{PPh}), 132.9 (d, $J_{\text{CP}}=3.1$ Hz, $\text{N}-\text{C}_{\text{Ar}}$), 146.8 (iPr- C_{Ar}), 147.2 (iPr- C_{Ar}). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 25 °C): $\delta=-73.6$ (d, $J_{\text{PP}}=12.9$ Hz, PPh₂), 38.4 (d, $J_{\text{PP}}=12.8$ Hz, $\text{C}=\text{C}-\text{P}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, CDCl_3 , 25 °C): $\delta=-15.5$ (dd, $J_{\text{SiP}}=69.7$ Hz, $J_{\text{SiP}}=104.4$ Hz, $\text{P}-\text{Si}-\text{P}$), 22.2 (d, $J_{\text{SiP}}=3.0$ Hz, SiCH_3).

Compound 8-B: To a mixture of **3** (0.49 g, 0.39 mmol) in fluorobenzene (2 mL) was added triethylsilane (62 μL , 0.39 mmol) at room temperature. After 1 h, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **8-B** as pale orange powder (0.43 g, Yield: 84%). Mp : 276 °C. (Major isomer, 80%): ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta=0.62$ (s, 3H, SiCH_3), 0.71 (s, 3H, SiCH_3), 0.73 (m, 3H, $\text{CH}_{2\text{Et}}$), 0.86 (m, 6H, $\text{CH}_{2\text{Et}}$), 0.88 (m, 9H, $\text{CH}_{3\text{Et}}$), 1.13 (d, $J_{\text{HH}}=6.7$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.18 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.26 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.29 (d, $J_{\text{HH}}=6.8$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.34 (d, $J_{\text{PH}}=1.2$ Hz, 9H, $\text{CH}_{3\text{IBu}}$), 1.39 (d, $J_{\text{HP}}=0.9$ Hz, 9H, $\text{CH}_{3\text{IBu}}$), 1.47 (m, 1H, $\text{CH}_{2\text{Norb}}$), 1.54 (dd, $J_{\text{HH}}=1.7$ Hz, $J_{\text{HP}}=9.2$ Hz, 1H,

CH₂Norb), 1.67 (m, 1H, CH₂Norb), 1.75 (m, 1H, CH₂Norb), 1.92 (m, 1H, CH₂Norb), 1.97 (m, 1H, CH₂Norb), 2.71 (m, 1H, CH₃Pr), 2.76 (m, 1H, CH₃bridgehead), 3.03 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₃Pr), 3.36 (s, 1H, CH₃bridgehead), 5.33 (dd, $J_{\text{HP}} = 17.8$ Hz, 1H, $J_{\text{HSi}} = 184.9$ Hz, SiH), 7.23 (m, 2H, CH_{Ar}), 7.38 (m, 1H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): $\delta = 3.7$ (d, $J_{\text{PC}} = 2.2$ Hz, SiCH₃), 4.1 (d, $J_{\text{PC}} = 1.8$ Hz, CH₂Et), 6.1 (SiCH₃), 8.2 (SiCH₃Et), 23.7 (CH₃Pr), 24.4 (CH₃Pr), 25.4 (CH₃Pr), 25.4 (CH₂Norb), 26.1 (CH₃Pr), 27.9 (CH₂Norb), 28.3 (CH₃Pr), 28.4 (CH₃Pr), 32.0 (d, $J_{\text{PC}} = 6.5$ Hz, CH₃Pr), 32.7 (d, $J_{\text{PC}} = 5.4$ Hz, CH₃Pr), 41.6 (CH₃bridgehead), 44.4 (d, $J_{\text{PC}} = 11.4$ Hz, CH₃bridgehead), 49.8 (d, $J_{\text{PC}} = 7.0$ Hz, CH₂Norb), 52.7 (C_t-Bu), 53.7 (C_t-Bu), 102.7 (d, $J_{\text{PC}} = 65.4$ Hz, P=C=N), 124.9 (CH_{Ar}), 125.6 (CH_{Ar}), 129.8 (CH_{Ar}), 133.5 (d, $J_{\text{PC}} = 3.9$ Hz, C_{Ar}), 136.3 (d, $J_{\text{CF}} = 243.8$ Hz, B-C_{Ar}), 138.3 (d, $J_{\text{CF}} = 245.0$ Hz, C_{Ar}), 146.4 (C_{Ar}), 147.0 (C_{Ar}), 148.3 (d, $J_{\text{CF}} = 237.5$ Hz, B-C_{Ar}), 191.5 (d, $J_{\text{PC}} = 26.4$ Hz, P=C=N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): $\delta = 49.4$ (s, Si-satellite: $J_{\text{SiP}} = 33.8$ Hz), ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): $\delta = -33.3$ (d, $J_{\text{SiP}} = 34.2$ Hz, Si-H), 20.5 (SiEt₃), 20.5 (d, $J_{\text{SiP}} = 3.5$ Hz, SiCH₃). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 25 °C): $\delta = -16.1$. ¹⁹F NMR (470 MHz, CDCl₃, 25 °C): $\delta = -132.5$ (m, B(C₆F₅)₄), -163.5 (t, $J_{\text{FF}} = 20.5$ Hz, B(C₆F₅)₄), -167.0 (t, $J_{\text{FF}} = 19.6$ Hz, B(C₆F₅)₄). (Minor isomer, 20%): ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.61$ (s, 3H, SiCH₃), 0.72 (s, 3H, SiCH₃), 0.86 (m, 6H, CH₂Et), 1.16 (d, $J_{\text{HH}} = 7.1$ Hz, 3H, CH₃Pr), 1.30 (d, $J_{\text{HH}} = 6.7$ Hz, 3H, CH₃Pr), 1.37 (d, $J_{\text{PH}} = 0.8$ Hz, 9H, CH₃Pr), 1.36 (d, $J_{\text{HP}} = 1.1$ Hz, 9H, CH₃Pr), 1.59 (m, 1H, CH₂Norb), 1.84 (m, 1H, CH₂Norb), 2.76 (m, 1H, CH₃bridgehead), 2.81 (m, 1H, CH₃Pr), 2.90 (sept, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr), 3.24 (m, 1H, CH₃bridgehead), 5.42 (dd, $J_{\text{HP}} = 17.8$ Hz, 1H, $J_{\text{HSi}} = 187.7$ Hz, SiH), 7.23 (m, 2H, CH_{Ar}), 7.38 (m, 1H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): $\delta = 3.6$ (d, $J_{\text{PC}} = 2.1$ Hz, SiCH₃), 3.9 (d, $J_{\text{PC}} = 1.8$ Hz, CH₂Et), 5.7 (SiCH₃), 8.0 (SiCH₃Et), 24.0 (CH₃Pr), 24.5 (CH₃Pr), 24.8 (CH₃Pr), 25.2 (d, $J_{\text{PC}} = 1.6$ Hz, CH₂), 25.8 (CH₃Pr), 27.8 (CH₂Norb), 28.5 (CH₃Pr), 28.8 (CH₃Pr), 32.1 (d, $J_{\text{PC}} = 6.4$ Hz, CH₃Pr), 32.8 (d, $J_{\text{PC}} = 5.4$ Hz, CH₃Pr), 41.7 (CH₃bridgehead), 44.7 (d, $J_{\text{PC}} = 10.6$ Hz, CH₃bridgehead), 49.2 (d, $J_{\text{PC}} = 4.6$ Hz, CH₂Norb), 52.8 (C_t-Bu), 53.6 (C_t-Bu), 101.0 (d, $J_{\text{PC}} = 65.3$ Hz, P=C=N), 125.0 (s, CH_{Ar}), 125.7 (CH_{Ar}), 129.9 (CH_{Ar}), 133.8 (d, $J_{\text{PC}} = 2.9$ Hz, C_{Ar}), 136.3 (d, $J_{\text{CF}} = 243.8$ Hz, C_{Ar}), 138.3 (d, $J_{\text{CF}} = 245.0$ Hz, C_{Ar}), 145.9 (C_{Ar}), 146.7 (C_{Ar}), 148.3 (d, $J_{\text{CF}} = 237.5$ Hz, C_{Ar}), 191.1 (d, $J_{\text{PC}} = 26.1$ Hz, P=C=N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): $\delta = 47.9$ (s, Si-satellite: $J_{\text{SiP}} = 41.9$ Hz). ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): $\delta = -33.9$ (d, $J_{\text{SiP}} = 41.7$ Hz, Si-H), 21.0 (SiEt₃), 20.4 (d, $J_{\text{SiP}} = 3.1$ Hz, SiCH₃).

Compound 8-C: In a J. Young NMR tube, to a solution of **3a** (100 mg, 0.069 mmol) in fluorobenzene (0.5 mL), pinacolborane (10 μ L, 0.069 mmol) was added and warmed at 70 °C. The color of solution changed from yellow to colorless within 5 min. Addition of excess pentane (ca. 1.5 mL) at room temperature leads to crystallization of **8-C**, giving the corresponding **8-C** as colorless crystals (92 mg, 87%). Mp: 179–180 °C (decomp.). (Major isomer, 90%): ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.60$ (s, 3H, SiCH₃), 0.68 (s, 3H, SiCH₃), 1.17 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr), 1.17 (s, 6H, CH₃Pr), 1.18 (s, 6H, CH₃Pr), 1.23 (d, $J_{\text{HH}} = 6.8$ Hz, 6H, CH₃Pr), 1.26 (overlapped, 3H, CH₃Pr), 1.34 (s, 18H, CH₃Pr), 1.56 (d, $J_{\text{HH}} = 9.1$ Hz, 1H, CH₂Norb), 1.66 (m, 1H, CH₂Norb), 1.82 (d, $J_{\text{HH}} = 9.0$ Hz, 1H, CH₂Norb), 1.86 (m, 1H, CH₂Norb), 1.92 (m, 1H, CH₂Norb), 1.96 (m, 1H, CH₂Norb), 2.74 (m, 1H, CH₃bridgehead), 2.82 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₃Pr), 2.92 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₃Pr), 3.34 (s, 1H, CH₃bridgehead), 5.29 (d, $J_{\text{HP}} = 24.3$ Hz, Si-satellite: $J_{\text{HSi}} = 212.3$ Hz, Si-H), 7.21–7.25 (m, 2H, CH_{Ar}), 7.37–7.40 (m, 1H, CH_{Ar}), 7.55 (s, 4H, P-CH₃Ar), 7.74 (s, 8H, o-CH₃Ar). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): $\delta = 3.7$ (d, $J_{\text{PC}} = 1.4$ Hz, SiCH₃), 4.9 (SiCH₃), 23.8 (CH₃Pr), 24.2 (CH₃Pr), 24.3 (CH₃Pr), 24.8 (CH₃Pr), 24.9 (CH₃Pr), 24.9 (CH₂Norb), 26.1 (CH₃Pr), 27.9 (CH₂Norb), 28.6 (CH₃Pr), 28.6 (CH₃Pr), 32.1 (d, $J_{\text{PC}} = 6.1$ Hz, CH₃Pr), 32.5 (d, $J_{\text{PC}} = 5.7$ Hz, CH₃Pr), 41.2 (CH₃bridgehead), 44.6 (d, $J_{\text{PC}} = 10.5$ Hz, CH₃bridgehead), 48.9 (d, $J_{\text{PC}} = 4.7$ Hz, CH₂Norb), 52.8 (C_t-Bu), 53.5 (C_t-Bu), 86.8 (C_{Bpin}), 100.5 (d, $J_{\text{PC}} = 70.6$ Hz, P=C=N), 117.6 (br sept, $J_{\text{CF}} = 3.8$ Hz, P-CH₃Ar), 124.7 (q, $J_{\text{CF}} = 272.5$ Hz, CF₃), 125.1 (2xCH_{Ar}), 129.6 (CH_{Ar}), 129.1 (qq, $J_{\text{CF}} = 31.5$ Hz, $J_{\text{CB}} = 2.6$ Hz, m-CH₃Ar), 132.7 (d, $J_{\text{PC}} = 2.6$ Hz, N-C_{Ar}), 135.0 (o-CH₃Ar), 146.2 (iPr-C_{Ar}), 146.6 (iPr-C_{Ar}), 161.9 (q, $J_{\text{CB}} = 49.8$ Hz, B-C_{Ar}), 192.6 (d, $J_{\text{PC}} = 25.7$ Hz, P=C=N). ³¹P

{¹H} NMR (202 MHz, CDCl₃, 25 °C): $\delta = 39.8$ (s, Si-satellite: $J_{\text{SiP}} = 111.0$ Hz, C=C-P). ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): $\delta = -35.0$ (br, P-Si), 19.9 (SiCH₃). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 25 °C): $\delta = -6.6$ (BAr₄), 30.3 (br, Bpin). ¹⁹F NMR (470 MHz, CDCl₃, 25 °C): $\delta = -62.4$ (CF₃). (Minor isomer, 40%): ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.60$ (overlapped, 3H, SiCH₃), 0.68 (overlapped, 3H, SiCH₃), 1.13 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr), 1.19 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr), 1.25 (overlapped, 3H, CH₃Pr), 1.25 (s, 6H, CH₃Pr), 1.26 (s, 6H, CH₃Pr), 1.31 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr), 1.33 (s, 9H, CH₃Pr), 1.37 (s, 9H, CH₃Pr), 1.52 (d, $J_{\text{HH}} = 8.5$ Hz, 1H, CH₂Norb), 1.74 (d, $J_{\text{HH}} = 8.5$ Hz, 1H, CH₂Norb), 2.74 (m, 1H, CH₃bridgehead), 2.72 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₃Pr), 3.06 (sept, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₃Pr), 3.37 (s, 1H, CH₃bridgehead), 5.14 (d, $J_{\text{HP}} = 18.6$ Hz, Si-satellite: $J_{\text{HSi}} = 211.9$ Hz, Si-H), 7.21–7.25 (m, 2H, CH_{Ar}), 7.37–7.40 (m, 1H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): $\delta = 3.7$ (d, $J_{\text{PC}} = 1.0$ Hz, SiCH₃), 5.1 (SiCH₃), 24.0 (CH₃Pr), 24.1 (CH₃Pr), 24.8 (CH₃Pr), 25.3 (CH₃Pr), 25.0 (d, $J_{\text{PC}} = 1.0$ Hz, CH₂Norb), 25.5 (CH₃Pr), 25.5 (CH₃Pr), 27.8 (CH₂Norb), 28.2 (CH₃Pr), 28.4 (CH₃Pr), 31.8 (d, $J_{\text{PC}} = 6.2$ Hz, CH₃Pr), 32.5 (d, $J_{\text{PC}} = 5.6$ Hz, CH₃Pr), 41.3 (CH₃bridgehead), 44.4 (d, $J_{\text{PC}} = 11.2$ Hz, CH₃bridgehead), 49.4 (d, $J_{\text{PC}} = 6.8$ Hz, CH₂Norb), 52.9 (C_t-Bu), 53.5 (C_t-Bu), 87.0 (C_{Bpin}), 101.7 (d, $J_{\text{PC}} = 69.4$ Hz, P=C=N), 125.2 (CH_{Ar}), 125.3 (CH_{Ar}), 129.8 (CH_{Ar}), 132.8 (d, $J_{\text{PC}} = 3.5$ Hz, N-C_{Ar}), 146.4 (iPr-C_{Ar}), 147.3 (iPr-C_{Ar}), 193.1 (d, $J_{\text{PC}} = 26.1$ Hz, P=C=N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): $\delta = 40.0$ (s, Si-satellite: $J_{\text{SiP}} = 110.8$ Hz, C=C-P). ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): $\delta = -32.3$ (br, detected by ¹H-²⁹Si HSQC, P-Si), 20.3 (SiCH₃).

Compound 9: To a mixture of **8-B** (0.30 g, 0.23 mmol) in fluorobenzene (1.8 mL) was added diisopropylformamide (3.3 μ L, 0.23 mmol) at room temperature. After 1 h, all volatiles were removed under vacuum. The residue was washed with pentane to obtain **9** as pale orange powder (0.26 g, Yield: 78%). Crystals suitable for X-ray diffraction analysis were obtained from a solution in CDCl₃/pentane at room temperature. (Major isomer, 69%): ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.23$ (m, 6H, CH₂Et), 0.75 (d, $J_{\text{HH}} = 8.0$ Hz, 9H, CH₃Et), 0.79 (s, 3H, SiCH₃), 0.80 (s, 3H, SiCH₃), 1.15 (d, $J_{\text{HH}} = 6.9$ Hz, 3H, CH₃Pr-Dip), 1.26 (d, $J_{\text{HH}} = 6.9$ Hz, 3H, CH₃Pr-Dip), 1.26 (d, $J_{\text{H}} = 6.9$ Hz, 6H, CH₃Pr-Dip), 1.29 (d, $J_{\text{HH}} = 6.8$ Hz, 6H, CH₃Pr-Dip), 1.31 (d, $J_{\text{HH}} = 6.8$ Hz, 6H, CH₃Pr-Dip), 1.36 (overlapped, 1H, CH₂Norb), 1.38 (overlapped, 1H, CH₂Norb), 1.42 (s, 9H, CH₃Pr), 1.43 (s, 9H, CH₃Pr), 1.58 (d, $J_{\text{HH}} = 6.8$ Hz, 1H, CH₂Norb), 1.77 (m, 1H, CH₂Norb), 1.84 (m, 1H, CH₂Norb), 1.89 (m, 1H, CH₂Norb), 2.54 (br s, 1H, CH₃bridgehead), 2.94 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH₃Pr-Dip), 2.98 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH₃Pr-Dip), 3.304 (brs, 1H, CH₃bridgehead), 3.40 (d, $J_{\text{HH}} = 6.6$ Hz, 2H, CH₃Pr-Dip), 4.06 (dd, $J_{\text{HP}} = 22.3$ Hz, $J_{\text{HH}} = 3.9$ Hz, PCH₃Pr-Dip), 5.55 (dd, $J_{\text{HP}} = 4.1$ Hz, $J_{\text{HH}} = 3.9$ Hz, Si-satellite: $J_{\text{HSi}} = 253.3$ Hz, Si-H), 7.22–7.27 (m, 2H, CH_{Ar}), 7.36–7.40 (m, 1H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): $\delta = 4.4$ (d, $J_{\text{PC}} = 3.1$ Hz, SiCH₃), 5.9 (CH₂Et), 6.6 (SiCH₃), 7.1 (SiCH₃Et), 22.6 (CH₃Pr-Dip), 23.3 (CH₃Pr-Dip), 24.1 (CH₃Pr-Dip), 24.2 (CH₃Pr-Dip), 24.5 (CH₃Pr-Dip), 25.4 (d, $J_{\text{PC}} = 2.3$ Hz, CH₂Norb), 26.0 (CH₃Pr-Dip), 27.7 (CH₂Norb), 28.6 (CH₃Pr-Dip), 29.1 (CH₃Pr-Dip), 31.7 (d, $J_{\text{PC}} = 4.8$ Hz, CH₃Pr), 33.1 (d, $J_{\text{PC}} = 5.5$ Hz, CH₃Pr), 44.4 (d, $J_{\text{PC}} = 6.0$ Hz, CH₃bridgehead), 46.8 (d, $J_{\text{PC}} = 12.1$ Hz, CH₃bridgehead), 47.5 (d, $J_{\text{PC}} = 4.7$ Hz, CH₂Norb), 51.5 (CH₃Pr-Dip), 54.1 (C_t-Bu), 54.4 (C_t-Bu), 54.9 (d, $J_{\text{PC}} = 53.4$ Hz, PCH₃Pr-Dip), 94.4 (d, $J_{\text{PC}} = 89.4$ Hz, P=C=N), 124.2 (br, B-C_{Ar}), 125.4 (CH_{Ar}), 125.6 (CH_{Ar}), 129.4 (CH_{Ar}), 135.3 (N-C_{Ar}), 136.4 (d, $J_{\text{CF}} = 244.0$ Hz, B-C_{Ar}), 138.3 (d, $J_{\text{CF}} = 244.3$ Hz, B-C_{Ar}), 146.0 (iPr-C_{Ar}), 146.8 (iPr-C_{Ar}), 148.4 (d, $J_{\text{CF}} = 242.5$ Hz, C_{Ar}), 178.1 (d, $J_{\text{PC}} = 13.5$ Hz, P=C=N). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): $\delta = 47.9$ (s, Si-satellite: $J_{\text{SiP}} = 41.9$ Hz), ²⁹Si{¹H} NMR (99 MHz, CDCl₃, 25 °C): $\delta = 20.5$ (d, $J_{\text{SiP}} = 5.7$ Hz, SiMe₂), 21.0 (SiEt₃), -33.9 (d, $J_{\text{SiP}} = 41.7$ Hz, SiH). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 25 °C): $\delta = -16.6$. ¹⁹F NMR (470 MHz, CDCl₃, 25 °C): $\delta = -132.5$ (m, B(C₆F₅)₄), -163.4 (t, $J_{\text{FF}} = 20.5$ Hz, B(C₆F₅)₄), -167.0 (t, $J_{\text{FF}} = 19.5$ Hz, B(C₆F₅)₄). (Minor isomer, 31%): ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.23$ (overlapped, 6H, CH₂Et), 0.76 (d, $J_{\text{HH}} = 8.1$ Hz, 9H, CH₃Et), 0.18 (s, 3H, SiCH₃), 0.82 (s, 3H, SiCH₃), 1.36 (d, $J_{\text{HH}} = 6.7$ Hz, 3H, CH₃Pr-NiPr₂), 1.39 (d, $J_{\text{HH}} = 6.8$ Hz, 3H, CH₃Pr-NiPr₂), 1.38 (s, 9H, CH₃Pr), 1.43 (s, 9H, CH₃Pr), 2.61 (br s, 1H, CH₃bridgehead), 2.87 (sept, $J_{\text{HH}} = 6.7$ Hz, 1H, CH₃Pr-Dip), 3.25 (br s,

${}^1\text{H}$, $\text{CH}_{\text{bridgehead}}$, 3.44 (sept, $J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}_{\text{NiPr}_2}$), 3.92 (dd, $J_{\text{HP}} = 20.5$ Hz, $J_{\text{HH}} = 3.6$ Hz, $\text{PCH}_{\text{NiPr}_2}$), 5.55 (dd, $J_{\text{HP}} = 6.7$ Hz, 1H, SiH), 7.22–7.27 (m, 2H, CH_{Ar}), 7.36–7.40 (m, 1H, CH_{Ar}). ${}^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C): $\delta = 4.6$ (d, $J_{\text{PC}} = 2.9$ Hz, SiCH_3), 5.9 (CH_2Et), 6.3 (SiCH_3), 7.0 (SiCH_3Et), 23.4 ($\text{CH}_{3\text{IPr-Dip}}$), 23.9 ($\text{CH}_{3\text{IPr-Dip}}$), 24.0 (CH_2Norb), 25.2 (br, $\text{CH}_3\text{-iNIPr}_2$), 25.3 ($\text{CH}_{3\text{IPr-Dip}}$), 25.4 ($\text{CH}_{3\text{IPr-Dip}}$), 25.8 ($\text{CH}_3\text{-iNIPr}_2$), 27.5 (CH_2Norb), 28.8 ($\text{CH}_{\text{IPr-Dip}}$), 29.0 ($\text{CH}_{\text{IPr-Dip}}$), 31.7 (d, $J_{\text{PC}} = 4.7$ Hz, $\text{CH}_{3\text{tBu}}$), 32.8 (d, $J_{\text{PC}} = 5.4$ Hz, $\text{CH}_{3\text{tBu}}$), 43.7 (d, $J_{\text{PC}} = 5.7$ Hz, $\text{CH}_{\text{bridgehead}}$), 46.8 (d, $J_{\text{PC}} = 12.1$ Hz, $\text{CH}_{\text{bridgehead}}$), 49.1 (d, $J_{\text{PC}} = 4.9$ Hz, CH_2Norb), 54.4 ($\text{CH}_{\text{IPr-NiPr}_2}$), 54.0 ($\text{C}_{\text{t-Bu}}$), 54.2 ($\text{C}_{\text{t-Bu}}$), 58.6 (d, $J_{\text{PC}} = 53.6$ Hz, $\text{PCH}_{\text{NiPr}_2}$), 94.5 (d, $J_{\text{PC}} = 89.0$ Hz, P-C-C-N), 125.4 (CH_{Ar}), 125.6 (CH_{Ar}), 129.6 (CH_{Ar}), 132.5 (N-C_{Ar}), 146.2 (iPr-C_{Ar}), 146.6 (iPr-C_{Ar}), 179.3 (d, $J_{\text{PC}} = 14.0$ Hz, P-C-C-N). ${}^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 25 °C): $\delta = 46.4$ (s, Si-satellite: $J_{\text{SiP}} = 77.4$ Hz). ${}^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, CDCl_3 , 25 °C): $\delta = 20.5$ (d, $J_{\text{SiP}} = 5.7$ Hz, SiMe_2), 21.0 (SiEt_3), -33.9 (d, $J_{\text{SiP}} = 41.7$ Hz, SiH).

Hydroboration of pyridine catalyzed by compound 8-C

In a J. Young NMR tube, to a solution of **8-C** (77 mg, 0.053 mmol) in fluorobenzene (0.5 mL), pinacolborane (77 μL , 0.553 mmol, 10 equiv.) and pyridine (44 μL , 0.553 mmol, 10 equiv.) was added and warmed at 60 °C. After 11 h, the consumption of HBpin was observed by ${}^{11}\text{B}$ NMR and formation of 1,4-hydroboration product was observed by ${}^1\text{H}$ NMR. After removal of all volatiles under reduced pressure, the residue was extracted by pentane and the filtrate were dried under reduced pressure to obtain the corresponding 1-pinacolboryl-1,4-dihydropyridine as colorless oil (102 mg, 90 %).

Data for **1-pinacolboryl-1,4-dihydropyridine**: ${}^1\text{H}$ NMR (300 MHz, 25 °C, C_6D_6): $\delta = 0.98$ (s, 2H, CH_3), 2.82 (m, 2H, CH_2), 4.57 (m, 2H, $\text{CH}_2\text{-CH}$), 6.50 (d, $J_{\text{HH}} = 8.1$ Hz, N-CH). ${}^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 25 °C, C_6D_6): $\delta = 22.8$ (CH_2), 24.6 (CH_3), 83.4 (O-C), 102.8 ($\text{CH}_2\text{-CH}$), 127.5 (N-CH). ${}^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, 25 °C, C_6D_6): $\delta = 23.9$ (Bpin). EI-MS Calculated for m/z $\text{C}_{11}\text{H}_{18}\text{BNO}_2$: 2017.1431, found: 207.1495.

Data for **10**: ${}^{31}\text{P}$ NMR (202 MHz, 25 °C, $\text{Ph-F/C}_6\text{D}_6$): $\delta = 108.6$ (t, $J_{\text{PH}} = 20.1$ Hz, N-P-Si). ${}^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, 25 °C, $\text{Ph-F/C}_6\text{D}_6$): $\delta = -20.4$ (d, $J_{\text{SiP}} = 10.5$ Hz, SiH_2B).

Reaction of compound 2-H with H_2

In a pressure NMR tube, the fluorobenzene solution (0.6 mL) of **2-H** (110 mg, 0.0357 mmol) were exposed to a 5 bar of H_2 and heated at 80 °C for 16 h. The reaction is monitored by NMR. The same reaction was also effectuated in another NMR tube at the same time. After the reaction completed, the solutions in the two tubes were combined in a NMR tube. After removal all volatiles, the addition of pentane leads to the slow precipitation of **22** at room temperature. The solution was filtered and the solids were washed with pentane to obtain **22** as yellow solid. Recrystallization of the obtained solid in fluorobenzene/pentane gave **16** (140 mg, 96 %) as yellow crystals. The separated organic phase were dried under reduced pressure to obtain the corresponding **15** (33 mg, 60 %) as colorless powder. Crystals suitable for X-ray diffraction analysis of **22** were grown from Et_2O /pentane solution.

Data for **21**: Mp. 85–87 °C (decomp.). ${}^1\text{H}$ NMR (500 MHz, 25 °C, CDCl_3): $\delta = 0.43$ (s, 3H, SiMe_2), 0.46 (s, 3H, SiMe_2), 1.00 (d, $J_{\text{HH}} = 7.9$ Hz, 1H, CH_2Norb), 1.19 (d, $J_{\text{HH}} = 6.9$ Hz, 63H, $\text{CH}_{3\text{IPr}}$), 1.19 (d, $J_{\text{HH}} = 6.9$ Hz, 6H, $\text{CH}_{3\text{IPr}}$), 1.22 (d, $J_{\text{HP}} = 0.9$ Hz, 9H, $\text{CH}_{3\text{tBu}}$), 1.22 (overlapped, 1H, CH_2Norb), 1.25 (d, $J_{\text{HP}} = 0.9$ Hz, 9H, $\text{CH}_{3\text{tBu}}$), 1.32 (d, $J_{\text{HH}} = 7.9$ Hz, 1H, CH_2Norb), 1.49 (m, 1H, CH_2Norb), 1.61 (m, 1H, CH_2Norb), 1.68 (m, 1H, CH_2Norb), 2.26 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.24 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH_{IPr}), 3.29 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH_{IPr}), 3.53 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 4.91 (d, $J_{\text{HP}} = 29.9$ Hz, Si-satellite: $J_{\text{HSi}} = 219.5$ Hz, SiH_2), 7.14–7.17 (m, 2H, CH_{Ar}), 7.26 (t, $J_{\text{HH}} = 7.6$ Hz, 1H, CH_{Ar}). ${}^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 25 °C,

CDCl_3): $\delta = 6.3$ (SiMe_2), 7.8 (d, $J_{\text{CP}} = 5.6$ Hz, SiMe_2), 23.6 ($\text{CH}_{3\text{IPr}}$), 23.8 ($\text{CH}_{3\text{IPr}}$), 25.0 ($\text{CH}_{3\text{IPr}}$), 25.5 ($\text{CH}_{3\text{IPr}}$), 26.5 (CH_2Norb), 27.8 (CH_{IPr}), 27.9 (CH_{IPr}), 28.1 (CH_2Norb), 32.3 (d, $J_{\text{CP}} = 5.6$ Hz, $\text{CH}_{3\text{tBu}}$), 32.7 (d, $J_{\text{CP}} = 5.8$ Hz, $\text{CH}_{3\text{tBu}}$), 41.7 (d, $J_{\text{CP}} = 1.2$ Hz, $\text{CH}_{\text{bridgehead}}$), 46.5 (d, $J_{\text{CP}} = 4.2$ Hz, $\text{CH}_{\text{bridgehead}}$), 46.8 (CH_2Norb), 50.6 (d, $J_{\text{CP}} = 10.5$ Hz, C_{tBu}), 50.9 (d, $J_{\text{CP}} = 13.3$ Hz, C_{tBu}), 123.4 (d, $J_{\text{CP}} = 48.6$ Hz, PC=CN), 123.9 (CH_{Ar}), 124.1 (CH_{Ar}), 127.2 (CH_{Ar}), 142.8 (N-C_{Ar}), 146.5 (iPr-C_{Ar}), 147.8 (iPr-C_{Ar}), 165.7 (d, $J_{\text{CP}} = 29.2$ Hz, PC=CN). ${}^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, CDCl_3): $\delta = 106.6$ (s). ${}^{31}\text{P}$ NMR (202 MHz, 25 °C, CDCl_3): $\delta = 106.6$ (q, $J_{\text{PH}} = 29.8$ Hz). ${}^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, 25 °C, CDCl_3): $\delta = 8.9$ (d, $J_{\text{SiP}} = 0.9$ Hz, SiMe_2), -42.7 (d, $J_{\text{SiP}} = 18.8$ Hz, N-Si-P). ${}^{29}\text{Si}$ NMR (99 MHz, 25 °C, CDCl_3): $\delta = 8.8$ (m, SiMe_2), -42.7 (dq, $J_{\text{SiH}} = 220.4$ Hz, $J_{\text{SiP}} = 18.8$ Hz, N-Si-P).

Data for **22**: Mp.: 222–226 °C (decomp.). ${}^1\text{H}$ NMR (500 MHz, 25 °C, CDCl_3): $\delta = 0.63$ (s, 3H, SiMe_2), 0.64 (s, 3H, SiMe_2), 1.11 (d, $J_{\text{HH}} = 7.0$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.12 (d, $J_{\text{HH}} = 7.0$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.17 (d, $J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.19 (d, $J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}_{3\text{IPr}}$), 1.30 (d, $J_{\text{HP}} = 0.9$ Hz, 9H, $\text{CH}_{3\text{tBu}}$), 1.30 (overlapped, 1H, CH_2Norb), 1.33 (d, $J_{\text{HP}} = 0.9$ Hz, 9H, $\text{CH}_{3\text{tBu}}$), 1.52 (dd, $J_{\text{HP}} = 1.3$ Hz, $J_{\text{HH}} = 9.1$ Hz, 1H, CH_2Norb), 1.63 (m, 1H, CH_2Norb), 1.72 (d, $J_{\text{HH}} = 9.0$ Hz, 1H, CH_2Norb), 1.86 (m, 1H, CH_2Norb), 1.90 (m, 1H, CH_2Norb), 2.71 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 2.78 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH_{IPr}), 2.92 (sept, $J_{\text{HH}} = 6.9$ Hz, 1H, CH_{IPr}), 3.32 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 5.11 (d, $J_{\text{HP}} = 26.4$ Hz, Si-satellite: $J_{\text{HSi}} = 261.7$ Hz, SiH_2), 7.20 (d, $J_{\text{HH}} = 7.8$ Hz, 1H, CH_{Ar}), 7.37 (t, $J_{\text{HH}} = 7.8$ Hz, 1H, CH_{Ar}), 7.54 (s, 4H, P-CH_{BAr}), 7.72 (m, 4H, o-CH_{BAr}). ${}^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 25 °C, CDCl_3): $\delta = 3.6$ (d, $J_{\text{CP}} = 1.0$ Hz, SiMe_2), 5.3 (SiMe_2), 23.7 ($\text{CH}_{3\text{IPr}}$), 24.0 ($\text{CH}_{3\text{IPr}}$), 24.7 (CH_2Norb), 25.0 ($\text{CH}_{3\text{IPr}}$), 25.1 ($\text{CH}_{3\text{IPr}}$), 28.0 (CH_{IPr}), 28.5 (CH_{IPr}), 28.7 (CH_2Norb), 32.2 (d, $J_{\text{CP}} = 6.2$ Hz, $\text{CH}_{3\text{tBu}}$), 32.3 (d, $J_{\text{CP}} = 6.1$ Hz, $\text{CH}_{3\text{tBu}}$), 41.4 ($\text{CH}_{\text{bridgehead}}$), 44.1 (d, $J_{\text{CP}} = 10.3$ Hz, $\text{CH}_{\text{bridgehead}}$), 48.5 (d, $J_{\text{CP}} = 6.4$ Hz, CH_2Norb), 53.1 (C_{tBu}), 53.1 (C_{tBu}), 99.1 (d, $J_{\text{CP}} = 76.5$ Hz, PC=CN), 117.6 (br sept, $J_{\text{CF}} = 3.8$ Hz, P-CH_{BAr}), 124.7 (q, $J_{\text{CF}} = 272.5$ Hz, CF_3), 125.1 (CH_{Ar}), 125.2 (CH_{Ar}), 129.1 (qq, $J_{\text{CB}} = 2.7$ Hz, $J_{\text{CF}} = 31.2$ Hz, m-C_{BAr}), 129.6 (CH_{Ar}), 132.1 (N-C_{Ar}), 135.0 (o-CH_{BAr}), 146.3 (iPr-C_{Ar}), 146.6 (iPr-C_{Ar}), 161.9 (q, $J_{\text{CB}} = 49.9$ Hz, $\text{ipso-C}_{\text{BAr}}$), 191.8 (d, $J_{\text{CP}} = 24.2$ Hz, PC=CN). ${}^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 25 °C, CDCl_3): $\delta = -6.5$ (BAR). ${}^{19}\text{F}$ NMR (470 MHz, 25 °C, CDCl_3): $\delta = -62.0$ (CF_3). ${}^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 25 °C, CDCl_3): $\delta = 34.0$ (Si-satellite: $J_{\text{PSi}} = 136.9$ Hz). ${}^{31}\text{P}$ NMR (121 MHz, 25 °C, CDCl_3): $\delta = 34.0$ (t, $J_{\text{PH}} = 29.2$ Hz). ${}^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, 25 °C, CDCl_3): $\delta = 17.6$ (d, $J_{\text{SiP}} = 3.7$ Hz, SiMe_2), -78.2 (d, $J_{\text{SiP}} = 202.4$ Hz, N-Si-P).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- [1] a) P. P. Power, *Nature* **2010**, *463*, 171; b) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389; c) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748.
- [2] a) G. H. Spikes, J. C. Fetting, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232; b) Y. Peng, M. Brynda, B. D. Ellis, J. C. Fetting, E. Rivard, P. P. Power, *Chem. Commun.* **2008**, *45*, 6042.
- [3] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439.
- [4] D. Wendel, T. Szilvasi, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 9156.
- [5] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124.
- [6] a) Y. Peng, B. D. Ellis, X. Wang, P. P. Power, *J. Am. Chem. Soc.* **2008**, *130*, 12268; b) A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Angew. Chem. Int. Ed.* **2013**, *52*, 568; c) A. V. Protchenko, K. H. Birj Kumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500; d) K. Inomata, T. Watanabe, Y. Miyazaki, H. Tobita, *J. Am. Chem. Soc.* **2015**, *137*, 11935; e) A. Rit, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2016**, *55*, 378.
- [7] Z. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fetting, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2031.
- [8] a) G. Kehr, S. Schwendemann, G. Erker, *Top. Curr. Chem.* **2012**, *332*, 45; b) D. W. Stephan, G. Erker, *Top. Curr. Chem.* **2013**, *332*, 85.
- [9] a) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740; b) J. Paradies, *Angew. Chem. Int. Ed.* **2014**, *53*, 3552; c) J. Paradies, *Synlett* **2013**, *24*, 777.
- [10] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400.
- [11] a) T. Sasamori, T. Sugahara, T. Agou, K. Sugamata, J.-D. Guo, S. Nagase, N. Tokitoh, *Chem. Sci.* **2015**, *6*, 5526; b) T. Sugahara, J.-D. Guo, T. Sasamori, S. Nagase, N. Tokitoh, *Angew. Chem. Int. Ed.* **2018**, *57*, 3499; c) T. Sugahara, J.-D. Guo, D. Hashizume, T. Sasamori, N. Tokitoh, *J. Am. Chem. Soc.* **2019**, *141*, 2263.
- [12] a) R. Rodriguez, D. Gau, Y. Contie, T. Kato, N. Saffon-Merceron, A. Baceiredo, *Angew. Chem. Int. Ed.* **2011**, *50*, 11492; b) R. Rodriguez, Y. Contie, D. Gau, N. Saffon-Merceron, K. Miqueu, J.-M. Sotiropoulos, A. Baceiredo, T. Kato, *Angew. Chem. Int. Ed.* **2013**, *52*, 8437; c) D. Wendel, W. Eisenreich, C. Jandl, A. Pöthig, B. Rieger, *Organometallics* **2016**, *35*, 1; d) S. Wang, M. L. McCrea-Hendrich, C. M. Weinstein, C. A. Caputo, E. Hoppe, J. C. Fetting, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2017**, *139*, 6586.
- [13] M.-A. Légaré, M.-A. Courtemanche, É. Rochette, F.-G. Fontaine, *Science* **2015**, *349*, 513.
- [14] Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran, H. W. Roesky, *J. Am. Chem. Soc.* **2016**, *138*, 2548.
- [15] N. Del Rio, M. Lopez-Reyes, A. Baceiredo, N. Saffon-Merceron, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 1365.
- [16] B. Rao, R. Kinjo, *Angew. Chem. Int. Ed.* **2020**, *59*, 3147.
- [17] A. Okorn, A. Jayaraman, L. Englert, M. Arrowsmith, T. Swoboda, J. Weigelt, C. Brunecker, M. Hess, A. Lamprecht, C. Lenczyk, M. Rangab, H. Braunschweig, *Chem. Sci.* **2022**, *13*, 7566.
- [18] C. Gerdes, W. Saak, D. Haase, T. Müller, *J. Am. Chem. Soc.* **2013**, *135*, 10353.
- [19] Gaspar, P. P. In Organosilicon Chemistry VI; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, **2005**; p 10.
- [20] P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, B. Neumann, H.-G. Stammer, *Science* **2004**, *305*, 849.
- [21] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065.
- [22] M. Driess, S. Yao, M. Brym, C. Van Wüllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 6730.
- [23] D. C. H. Do, A. V. Protchenko, M. A. Fuentes, J. Hicks, P. Vasko, S. Aldridge, *Chem. Commun.* **2020**, *56*, 4684.
- [24] S. Yao, Y. Xiong, C. van Wüllen, M. Driess, *Organometallics* **2009**, *28*, 1610.
- [25] Y. Xiong, S. Yao, S. Inoue, E. Irran, *Driess, Angew. Chem. Int. Ed.* **2012**, *51*, 10074.
- [26] a) T. Agou, N. Hayakawa, T. Sasamori, T. Matsuo, D. Hashizume, N. Tokitoh, *Chem. Eur. J.* **2014**, *20*, 9246; b) Y. Li, Y.-C. Chan, Y. Li, I. Purushothaman, S. De, P. Parameswaran, C.-W. So, *Inorg. Chem.* **2016**, *55*, 9091; c) A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2013**, *52*, 6974; d) Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147; e) S. U. Ahmad, T. Szilvasi, S. Inoue, *Chem. Commun.* **2014**, *50*, 12619.
- [27] H.-X. Yeong, H.-W. Xi, Y. Li, K. H. Lim, C.-W. So, *Chem. Eur. J.* **2013**, *19*, 11786.
- [28] B.-X. Leong, J. Lee, Y. Li, M.-C. Yang, C.-K. Siu, M.-D. Su, C.-W. So, *J. Am. Chem. Soc.* **2019**, *141*, 17629.
- [29] B.-X. Leong, Y.-C. Teo, C. Condamin, M.-C. Yang, M.-D. Su, C.-W. So, *ACS Catal.* **2020**, *10*, 14824.
- [30] a) D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, F. P. Cossio, A. Baceiredo, *Chem. Eur. J.* **2010**, *16*, 8255; b) D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, A. Baceiredo, *J. Am. Chem. Soc.* **2010**, *132*, 12841; c) R. Rodriguez, T. Troadec, T. Kato, N. Saffon-Merceron, J.-M. Sotiropoulos, A. Baceiredo, *Angew. Chem. Int. Ed.* **2012**, *51*, 7158.
- [31] R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossio, A. Baceiredo, *Angew. Chem. Int. Ed.* **2011**, *50*, 10414.
- [32] R. Rodriguez, Y. Contie, D. Gau, N. Saffon-Merceron, K. Miqueu, J.-M. Sotiropoulos, A. Baceiredo, *T. Kato, Angew. Chem. Int. Ed.* **2013**, *52*, 8437.
- [33] a) R. Rodriguez, Y. Contie, R. Nougé, A. Baceiredo, N. Saffon-Merceron, J.-M. Sotiropoulos, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 14355; b) R. Rodriguez, Y. Contie, Y. Mao, N. Saffon-Merceron, A. Baceiredo, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2015**, *54*, 15276.
- [34] D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossio, A. Baceiredo, *Angew. Chem. Int. Ed.* **2010**, *49*, 6585.
- [35] a) J. I. Schweizer, M. G. Scheibel, M. Diefenbach, F. Neumeyer, C. Würtele, N. Kulinskaya, R. Linser, N. Auner, S. Schneider, M. C. Holthausen, *Angew. Chem. Int. Ed.* **2016**, *55*, 1782; b) M. W. Stanford, J. I. Schweizer, M. Menche, G. S. Nichol, M. C. Holthausen, M. J. Cowley, *Angew. Chem. Int. Ed.* **2019**, *58*, 1329.
- [36] C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948.
- [37] Deposition Numbers "https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202202037" CCDC-2182214 (for **2-H**), CCDC-2182213 (for **3a**), CCDC-2182212 (for **3b**), CCDC-2182211 (for **3c**), CCDC-2182208 (for **3d**), CCDC-2182210 (for **5**), CCDC-2182209 (for **6-A**), CCDC-2182207 (for **6-B**), CCDC-2182205 (for **7**), CCDC-2182206 (for **9**) and CCDC-2182215 (for **22**) 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 <http://www.ccdc.cam.ac.uk/structures> "Access Structures service".
- [38] A. Dajnak, E. Maerten, N. Saffon-Merceron, A. Baceiredo, T. Kato, *Organometallics* **2020**, *39*, 3403.
- [39] S. Usman Ahmad, T. Szilvasi, E. Irran, S. Inoue, *J. Am. Chem. Soc.* **2015**, *137*, 5828.
- [40] A similar reactivity of phosphine-stabilized silylene toward an iminium salt has been already observed: I. Alvarado-Beltran, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 16141.
- [41] Other examples of hydroboration of pyridine catalyzed by non-metallic catalysts: a) X. Fan, J. Zheng, Z. H. Li, H. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 4916; b) E. N. Keyzer, S. S. Kang, S. Hanf, D. S. Wright, *Chem. Commun.* **2017**, *53*, 9434; c) B. Rao, C. C. Chong, R. Kinjo, *J. Am. Chem. Soc.* **2018**, *140*, 652–656; d) B.-X. Leong, J. Lee, Y. Li, M.-C. Yang, C.-K. Siu, M.-D. Su, C.-W. So, *J. Am. Chem. Soc.* **2019**, *141*, 17629; e) N. Sarkar, S. Bera, S. Nembenna, *J. Org. Chem.* **2020**, *85*, 4999; f) C. Hu, J. Zhang, H. Yang, L. Guo, C. Cui, *Inorg. Chem.* **2021**, *60*, 14038.
- [42] X. Fan, J. Zheng, Z. Hua Li, H. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 4916.
- [43] FLP involving silylium ion and/or silylene: a) Z. Dong, Z. Li, X. Liu, C. Yan, N. Wei, M. Kira, T. Müller, *Chem. Asian J.* **2017**, *12*, 1204; b) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtman, T. Müller, *Chem. Eur. J.* **2014**, *20*, 9381; c) A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 12636; d) M. Reißmann, A. Schäfer, S. Jung, T. Müller, *Organometallics* **2013**, *32*, 6736.

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