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Synthesis of Norbornene Based-Phosphine-Stabilized Silylium Ions Behaving as Masked Frustrated Lewis Pairs.

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ABSTRACT: A novel architecture of phosphine-stabilized silylium ions is described. The peculiar moderate flexible framework allows an efficient donation of the phosphine group toward the electron deficient silicon center thus providing a very good stabilization of the corresponding silylium ions. The P-Si interaction was studied in solution and in the solid state by NMR spectroscopy and X-ray diffraction analysis, respectively. The reactivity of silylium ions is easily improved using less donating phosphine ligands. Of particular interest, thanks to the flexible ligand framework, phosphine-stabilized silylium ion **5f** behaves as a frustrated Lewis pair instead of a simple Lewis acid and exhibits an original ambiphilic reactivity with carbonyl derivatives that allows the synthesis of seven- to nine-membered ring heterocycles.

With the synthesis of the first free silylium ion **I**, the groups of Reed and Lambert have achieved a major synthetic challenge.¹ Indeed, because of their exceptionally high Lewis acidity, silylium ions have remained for a long time elusive species.² To take advantage of these unique species in synthesis or catalysis, their reactivity needs to be tamed.³ The study of these species has been facilitated by the use of a Lewis Base that can intramolecularly interact with the silylium center, to afford a good balance between reactivity and stability (**II**, Figure 1).⁴ Following this strategy, several different types of donor groups have been introduced to achieve this intramolecular stabilization (**III-VI**, Figure 1).

The applications of these species have generated great deal of interest in recent years, especially in the field of catalysis. For instance, hydrodefluorination (HDF) reactions of alkylfluorides were found to be efficiently catalyzed by intramolecularly stabilized silyl cations **III**, **IV** and **V**.⁵ These species are also capable of catalyzing Diels-Alder reactions, and the ferrocene-stabilized system **VI** developed by Oestreich group is particularly efficient for the low-temperature cycloaddition reactions with α,β -unsaturated ketones.⁶ Interestingly, triarylsilylium ions such as **I** have been used for the rational design of new frustrated Lewis pair (FLP) systems able to activate dihydrogen and to sequester carbon dioxide.⁷

One of our main objectives is the stabilization of electron deficient species,⁸ and recently, a framework based on norbornene was designed to stabilize silylenes using phosphines as Lewis base.⁹ Of special interest, we have shown that, due to the weak coordination of phosphine ligand, phosphine-stabilized silylenes remain highly reactive. Moreover, they present, to some extent, "transition metal-like behavior" as demonstrated by the reversible binding of ethylene to the Si(II) center¹⁰ and the reversible oxidation addition/reductive elimination of R_3SiH at the Si(II) center.¹¹ The key features of this system are the moderate structural flexibility as well as the rigid planar structure of the enamino phosphine fragment, which results in a particular P→Si interaction. We have thus considered the synthesis of the novel phosphine-stabilized silylium ions **4**, which despite of a strong P-Si interaction behave as frustrated Lewis pairs and allows the synthesis of seven- to nine-membered heterocycles.

Figure 1. First free silylium ion and intramolecularly stabilized silylium ions.

A straightforward synthesis of the silylium precursors, the silylated amino(phosphino) derivatives **2**, has been developed from the corresponding iminophosphines **1** (Scheme 1).⁹

Scheme 1. Synthesis of silylium precursors **2**.

Attempts to generate silylium ions *via* the classical Bartlett-Schneider-Condon method² using trityl tetrakis(pentafluorophenyl)borate have failed. Rather than the hydride abstraction, the phosphonium salt **3** was obtained nearly quantitatively, by the reaction of the trityl cation at the 4-position of a phenyl group (Scheme 2). The same type of reaction between bulky phosphines (P*t*Bu₃ or PCy₃) and trityl salts was already observed by Stephan et al..¹²

Scheme 2. Reaction of **2a** with trityl cation.

Phosphonium salt **3** was fully characterized by NMR spectroscopy and its structure was confirmed by X-Ray diffraction analysis (Figure 2). The P1-C32 bond length is classical for a single bond, and the cyclohexadiene ring shows alternate single and double bond lengths, planar environments around C35 and C38 (respectively $\Sigma^\circ = 359.9$ and 360.0°) and a tetrahedral environment at C32.

Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30 % probability. H atoms (except on Si1 and C32), solvent molecules and counterion [B(C₆F₅)₄][−] were omitted for clarity. Selected bond lengths [Å]: P1-C1 1.777(2), C1-C2 1.380(3), C2-N1 1.391(3), N1-C18 1.463(3), P1-C32 1.841(2), C32-C33 1.493(3), C33-C34 1.337(4), C34-C35 1.463(3), C35-C36 1.460(4), C36-C37 1.339(4), C37-C32 1.508(3), C35-C38 1.372(3), C38-C39 1.486(4), C38-C45 1.484(3).

The expected silylium ions **4** can be easily obtained following the Kira's and Sakurai's methodology,¹³ starting from the corresponding chlorosilanes **2b-e**, just by halide abstraction using potassium borate salt (Scheme 3).

Scheme 3. Preparation of silylium ions **4b-e** and **5f,g**.

In order to study the phosphorus-silicon interaction, several silylium ions were prepared (**4b-e**), and characterized in solution and in the solid state. The main spectroscopic data are summarized in Table 1.

Table 1. NMR data of silylium ions **4b-e** (in CD₂Cl₂ at 298 K).

Cpd	R ²	R ³	³¹ P	²⁹ Si	J _{PSi} [Hz]
4b	Me	Me	39.6	6.1	132.0
4c ^[a]	Cl	Me	30.2 and 30.0	-0.3 and -2.1	172.6 and 171.2
4d ^[b]	Cl	H	28.4	-22.9	169.5
4e	Cl	Cl	21.8	-21.6	237.4

Cpd = compound; [a] d.r. = 50:50. [b] only one diastereomer is formed. Chemical shift in ppm and coupling constants in Hz.

Silylium ions **4c** and **4d** with two different substituents on the Si atom (**4c**: R² = Cl, R³ = Me, **4d**: R² = Cl, R³ = H) were

expected to be formed as diastereomer couples since the silylium center is stereogenic. A 50:50 diastereomeric ratio was obtained for **4c** but in the case of **4d**, a single diastereomer is formed. Regarding the strong phosphine-silylium ion interaction (*vide infra*), the epimerization of **4** at the chiral silicon center through the P-Si bond dissociation is difficult to be considered. Instead, the diastereoselective formation of **4d** is probably due to a selective Cl-abstraction from **2d** featuring a pentacoordinate Si center bearing two different Cl atoms (apical and equatorial positions). Indeed, the pentacoordinate nature of the Si atom in **2d** with a strong P→Si interaction, was clearly indicated by the significantly highfield-shifted signals in ^{29}Si - and ^{31}P -NMR (^{29}Si : -87.2 ppm, ^{31}P : 43.1 ppm) with a large $J_{\text{Si-P}}$ coupling constant (223.8 Hz) compared to those observed for **2c** showing typical silane and phosphine signals (^{29}Si : -5.5 ppm, ^{31}P : 111.3 ppm) in agreement with a tetracoordinate Si atom without P→Si interaction (Scheme 4). Note that, **2d** exists as a single diastereomer presenting a pentacoordinate Si center with a strongly electron-withdrawing Cl atom at the apical position and another Cl atom at the less-hindered equatorial position. The formation of **4d** should exclusively takes place, keeping the configuration at the Si center, *via* the cleavage of more strongly polarized apical Si-Cl bond in **2d**, which explains the high diastereoselectivity of the reaction. In contrast, in the case of **2c**, due to the free-rotation at the N-Si bond axis because of the absence of P→Si interaction, the abstraction of Cl anion is not selective and, thus, affords **4c** as a mixture of two diastereomers.

Scheme 4. ^{29}Si - and ^{31}P -NMR chemical shifts of **2c** and **2d** and the diastereoselective formation of **4d**.

The analysis of these spectroscopic data indicates that silylium **4e**, which bears two strong electron-withdrawing chloride atoms, shows the strongest P-Si interaction as indicated by a relatively shielded ^{31}P NMR chemical shift ($\delta = 21.8$ ppm) and a large silicon-phosphorus coupling constant ($J_{\text{PSi}} = 237.4$ Hz). The ^{29}Si NMR chemical shift is also a good probe to evaluate the Lewis acidity of silylium ions.¹⁴ In this series, **4b** exhibits an enhanced Lewis acidity as indicated by the ^{29}Si NMR chemical shift which appears at $\delta = 6.1$ ppm, among the more deshielded signals and the smallest silicon-phosphorus coupling constant ($J_{\text{PSi}} = 132.0$ Hz). The four silylium ions **4b-e** synthesized were also characterized, in the solid state, by X-ray diffraction analysis (Figure 3 and Table 2).

Figure 3. Molecular structure of **4b**, **4c**, **4d** and **4e**. Thermal ellipsoids represent 30 % probability. Counter ions, solvent molecules, disordered atoms and hydrogen atoms were omitted for clarity (except the hydrogen atom on the silicon atom of **4d**).

Table 2. Main bond lengths (in Å) obtained from X-Ray diffraction analysis of **4b-4e**.

Cpd	P1C1	C1C2	C2N1	N1Si1	Si1P1	Si1R ²	Si1R ³
4b	1.730 (3)	1.369 (4)	1.371 (4)	1.781 (3)	2.322 (1)	1.844 (4) Si-CH ₃	1.844 (4) Si-CH ₃
4c	1.708 (12)	1.383 (16)	1.423 (16)	1.731 (11)	2.302 (7)	1.952 (13) Si-Cl	1.73 (3) Si-CH ₃
4d	1.737 (9)	1.370 (10)	1.355 (6)	1.734 (4)	2.287 (2)	2.067 (2) Si-Cl	1.44 (8) Si-H
4e	1.711 (4)	1.368 (5)	1.368 (4)	1.730 (3)	2.293 (1)	2.014 (1) Si-Cl	2.011 (1) Si-Cl

The X-Ray diffraction data are in good agreement with the spectroscopic data. Indeed, the longest Si1P1 bond length [2.322(1) Å] of the series was found in **4b**, suggesting a weak Si-P interaction, in other words, the stronger Lewis acid of the series. Noteworthy, the modification of the silylium center substituent (R² and R³) has a rather weak impact on the Si-P interaction.

In order to reduce the Si-P interaction, we have considered the use of a less electron donating phosphine fragment. Therefore, the cyclic diaminophosphino group was replaced by a diphenylphosphino moiety, and the corresponding silylium ions

5f,g ($\text{PR}_2 = \text{PPh}_2$) have been prepared using the same synthetic methodology as for **4** (Scheme 3).

The new silylium ions **5** were obtained in nearly quantitative yields, and in the case of **5g** ($\text{R}^2 = \text{Cl}$, $\text{R}^3 = \text{Me}$) as a mixture of two diastereomers in a 76:24 ratio. The spectroscopic data are summarized in Table 3. As expected, the weaker donation of the diphenylphosphino group is evidenced by deshielded ^{29}Si NMR signals at $\delta = 27.2$ ppm for **5f** and $\delta = 15.4$ and 15.3 ppm for **5g** compared to those observed for the corresponding silylium ions **4b,c** stabilized by a more strongly electron donating diaminophosphino ligand (**4b**: $\delta = 6.1$ ppm, **4c**: $\delta = -0.3$ and -2.1 ppm). Again, the smallest J_{PSi} coupling constant is observed for silylium **5f** ($\text{R}^2 = \text{R}^3 = \text{Me}$).

Table 3. Experimental NMR parameters of silylium ions **5f-g** (in CD_2Cl_2 at 298 K).

Cpd	R^2	R^3	^{31}P	^{29}Si	J_{PSi} [Hz]
5f	Me	Me	-20.8	27.2	82.1
5g ^[a]	Cl	Me	-24.3 and -24.1	15.4 and 15.3	124.6 and 117.4

Cpd = compound; [a] d.r. = 76:24. Chemical shift in ppm and coupling constants in Hz.

Although, the ability of these two families of silylium ions as catalyst of Diels Alder reaction between cyclohexadiene or 2,3-dimethylbutadiene and methyl acrylate (10 mol% of silylium **4** or **5** in CDCl_3)^{4a, 6, 15} was tested, no trace of the expected cycloadducts could be detected by NMR spectroscopy, after several hours at 80 °C. Interestingly, in the case of **5f**, the ^{31}P NMR analysis shows the complete disappearance of the silylium signal (-20.8 ppm) and a new single signal appeared at $\delta = 20.9$ ppm. In fact, silylium ion **5f** reacts with one equivalent of methyl acrylate at 50 °C, leading to an insertion reaction of the conjugated carbonyl into the $\text{P} \rightarrow \text{Si}$ dative bond. Silylium cation **5f**, acting as a frustrated Lewis pairs (FLP),^{7b,16} affords quantitatively an original 9-membered heterocycle **6**, which loses the Lewis acid character (silane structure), probably explaining the absence of any catalytic activity (Scheme 5).

Scheme 5. Reaction of silylium ion **5f** with carbonyl derivatives.

The ^{13}C NMR is particularly informative with the peculiar chemical shift of the ketene acetal type part $\text{CH}=\text{C}$ of **6**, chemical shift at $\delta = 67.8$ ppm ($J_{\text{CP}} = 10.6$ Hz) for primary- and at $\delta = 156.9$ ppm ($J_{\text{CP}} = 5.5$ Hz) for the quaternary-carbon atoms respectively. In the same vein, we observed at room temperature, the immediate and quantitative insertion of benzaldehyde into the Si-P bond of silylium **5f**.¹⁷ The corresponding 7-membered ring **7** was isolated as a mixture of two diastereomers in a 68:32 ratio, and fully characterized by NMR spectroscopy and

the structure was confirmed by X-ray diffraction analysis (Figure 4). The high reactivity of **5f** as a masked FLP can be explained by the weak $\text{P} \rightarrow \text{Si}$ interaction as well as the moderate flexibility of ligand framework. Indeed, such a flexibility of ligand was clearly confirmed by the significantly elongated P1-Si1 distance (3.624 Å in **7** vs 2.322 Å in **4b**) and the associated wide interior angles of P1-C1-C2-N1-Si1 fragment (P1-C1-C2 132.36° , C1-C2-N1 130.78° and C2-N1-Si1 122.63°) in **7**, compared with those of the phosphine-silylium ion complex **4b** (P1-C1-C2 116.82° , C1-C2-N1 125.50° and C2-N1-Si1 113.84°). However, **5f** is not enough reactive to activate H_2 as observed for the previously reported frustrated Lewis pairs constituted of free-silylium ion and a bulky phosphine. It should be noted that, in contrast to our system, the phosphine-stabilized silylium ion with a naphthalene-based rigid ligand framework (Type **V** in Figure 1) is very stable and no reactivity of such species has been described to date.¹⁸ Similar FLP type reactions were also observed for phosphine-stabilized germylene and stannylens with a strained three-membered cyclic structure.¹⁹

Figure 4. Molecular structure of **7**. Thermal ellipsoids represent 30 % probability. Counter ion, disordered atoms and hydrogen atoms were omitted for clarity (except H34). Selected bond lengths [Å] and angles [$^\circ$]: P1-C1 $1.746(2)$, C1-C2 $1.363(3)$, C2-N1 $1.386(2)$, N1-Si1 $1.763(2)$, Si1-C32 $1.841(3)$, Si1-C33 $1.844(2)$, Si1-O1 $1.650(2)$, C34-O1 $1.393(2)$, P1-C34 $1.864(2)$, C34-C35 $1.509(3)$; P1-C1-C2 $132.36(15)$, C1-C2-N1 $130.78(17)$, C2-N1-Si1 $122.63(13)$, N1-Si1-O1 $108.17(7)$, Si1-O1-C34 $129.51(13)$, O1-C34-P1 $103.54(13)$, C34-P1-C1 $109.32(9)$.

The reactions leading to the formation of cyclic phosphonium borates **6** and **7** are not reversible. Indeed, no evolution occurs after prolonged heating of the reaction mixtures. These adducts are so stable that silylium **5f** could not be regenerated when additional reactants such as phenylsilane were added.

In conclusion, a new type of phosphine-stabilized-silylium ion, based on a norbornene scaffold, was described. As expected, the moderate structural flexibility favours the enamino phosphine donation to electrophilic silicon center, affording stable silylium ions. Phosphine-silicon interactions were studied both in solution and in the solid state. The reactivity of silylium ions is easily improved using a weaker donating phosphine ligand. Of particular interest, thanks to the flexible ligand framework, and despite of an efficient intramolecular stabilization, the base-stabilized silylium ions **5f** behaves as frustrated Lewis pairs and allows the synthesis of seven- to nine-membered heterocycles. Further structural modifications are actually being

performed to improve the potential of this new class of silylium ions.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques or high-pressure NMR tube techniques. Dry and oxygen-free solvents were used. ^1H , ^{11}B , ^{13}C , ^{19}F , ^{28}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 parts per million (ppm) relative to Me_4Si as internal standard. ^{11}B NMR downfield chemical are expressed in ppm relative to $\text{BF}_3\cdot\text{Et}_2\text{O}$. ^{19}F -chemical shifts were reported in ppm relative to CFCl_3 as an external standard. ^{31}P NMR chemical shifts are expressed in ppm relative to 85 % H_3PO_4 . 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. Mass spectra were recorded on Hewlett Packard 5989A spectrometer. All commercially available reagents were used without further purification otherwise noted.

Synthesis of 1: $\text{PR}_2 = \text{P}(\text{NtBu})_2\text{SiMe}_2$. To a stirred solution of imine²⁰ (10.0 g, 37.1 mmol) in 80 mL of THF at -78°C was added *n*-butyllithium (1.6 M, 24.3 mL, 38.9 mmol) and the mixture was allowed to warm up to room temperature over 1 h under stirring. The solution was cooled to -78°C and chlorophosphine (9.9 g, 37.1 mmol) was added. The mixture was allowed to warm up to room temperature and the solvent was removed under vacuum. The solid was washed with acetonitrile (3 x 20 mL), dried and dissolved with pentane, and then filtered. The volatile substances were removed under vacuum, and compound **1** (17.4 g, 94 %) was obtained as a white solid. Spectroscopic data of **1** are in perfect agreement with the values already reported.²⁰ $\text{PR}_2 = \text{PPh}_2$. To a solution of imine (10.00 g, 37.1 mmol) in THF (80 mL) was added dropwise at -80°C a solution of *n*-butyllithium 1.6 M in hexane (23.2 mL, 37.1 mmol) and stirred for 1 h. The reaction mixture was warmed up to room temperature and stirred for 1 h, then cooled again to -80°C and chlorodiphenylphosphine (6.84 mL, 37.1 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h, then the solvent was removed under vacuum. Product **1** was extracted with pentane. After evaporation of the solvent, the solid was washed with a minimum of acetonitrile to give **1** as a white powder (11.08 g, 66 % yield). Spectroscopic data of **1** are in perfect agreement with the values already reported.²¹

Synthesis of 2a ($\text{R}^1 = \text{H}$; $\text{R}^2 = \text{R}^3 = \text{Me}$): To a solution of iminophosphine **1** (2.00 g, 4.0 mmol) in THF (25 mL) was added dropwise at -80°C a solution of *n*-butyllithium 1.6 M in hexane (2.5 mL, 4.0 mmol) and stirred for 1 h. The reaction mixture was warmed up to room temperature and stirred for 1 h, then cooled again to -80°C and chlorodimethylsilane (0.44 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h, then the solvent was removed under vacuum. Product **2a** was extracted with heptane from the crude and pale-yellow crystals were obtained from a saturated heptane solution at -30°C (1.20 g, 54 % yield). ^1H NMR (300 MHz, C_6D_6): $\delta = 7.15\text{--}7.01$ (m, 3H, CH_{dipp}), 5.55 (dsept., $^2J_{\text{PH}} = 15.3$ Hz, $^3J_{\text{H-H}} = 2.7$ Hz, 1H, SiH), 3.86 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.43 (sept., $^3J_{\text{HH}} = 6.9$ Hz, 1H, CH_{IPr}), 3.32 (sept., $^3J_{\text{HH}} = 6.8$ Hz, 1H, CH_{IPr}), 2.56 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 1.98–1.71 (m, 2H, CH_2), 1.58–1.47 (m, 1H, CH_2), 1.47–1.38 (m, 2H, CH_2), 1.34 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.32 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.28–1.16 (m, 12H, $\text{CH}_3(\text{IPr})$), 1.10–1.03 (m, 2H, CH_2), 0.56 (dd, $^3J_{\text{HH}} = 2.8$ Hz, $^3J_{\text{PH}} = 4.4$ Hz, 3H, SiH- CH_3), 0.50 (s, 6H, Si- CH_3), 0.14 (dd, $^3J_{\text{HH}} = 3.2$ Hz, $^3J_{\text{PH}} = 1.9$ Hz, 3H, SiH- CH_3). ^{13}C NMR (75 MHz, C_6D_6): $\delta = 163.9$ (d, $^2J_{\text{CP}} = 26.5$ Hz, N-C), 147.9 (s, C_{dipp}), 147.0 (s, C_{dipp}), 142.3 (s, N- C_{dipp}), 127.4 (s, CH_{dipp}), 124.4 (s, CH_{dipp}), 124.2 (s, CH_{dipp}), 120.1 (d, $^1J_{\text{CP}} = 56.5$ Hz, C-P), 50.9 (d, $^2J_{\text{CP}} = 13.7$ Hz, C_{IBu}), 50.7 (d, $^2J_{\text{CP}} = 11.3$ Hz, C_{IBu}), 48.1 (d, $^2J_{\text{CP}} = 3.5$ Hz, $\text{CH}_{\text{bridgehead}}$), 47.0 (s, CH_2), 42.9 (s, $\text{CH}_{\text{bridgehead}}$), 32.7 (d, $^3J_{\text{CP}} = 4.9$ Hz, $\text{CH}_3(\text{Bu})$), 32.5 (d, $^3J_{\text{CP}} = 5.2$ Hz, $\text{CH}_3(\text{Bu})$), 28.8 (s, CH_2), 27.9 (s, 2 CH_{IPr}), 26.8 (s, CH_2), 25.3 (s, $\text{CH}_3(\text{IPr})$), 25.1 (s, $\text{CH}_3(\text{IPr})$), 24.8 (s, $\text{CH}_3(\text{IPr})$), 24.6 (s, $\text{CH}_3(\text{IPr})$), 8.0

(d, $^3J_{\text{CP}} = 5.3$ Hz, Si- CH_3), 6.3 (s, Si- CH_3), 0.3 (d, $^2J_{\text{CP}} = 24.5$ Hz, SiH- CH_3), 0.0 (d, $^2J_{\text{CP}} = 12.5$ Hz, SiH- CH_3). ^{31}P NMR (121 MHz, C_6D_6): $\delta = 114.5$ (d, $^2J_{\text{PH}} = 15.3$ Hz). ^{29}Si NMR (60 MHz, C_6D_6): $\delta = 8.1$ (s, SiMe_2), -9.2 (d, $^1J_{\text{SiP}} = 15.8$ Hz, SiMe_2H). M.p. = 209°C .

Synthesis of 2b ($\text{R}^1 = \text{Cl}$; $\text{R}^2 = \text{R}^3 = \text{Me}$): To a solution of iminophosphine **1** ($\text{PR}_2 = \text{cyclic diaminophosphine}$) (2.00 g, 4.0 mmol) in THF (20 mL) was added dropwise at -80°C a solution of *n*-butyllithium 1.6 M in hexane (2.5 mL, 4.0 mmol) and stirred for 1 h. The reaction mixture was warmed up to room temperature and stirred for 1 h, then cooled again to -80°C and dichlorodimethylsilane (0.48 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h, then the solvent was removed under vacuum. Product **2b** was extracted with heptane and colorless crystals were obtained from a saturated heptane solution at -30°C (1.45 g, 61 % yield). ^1H NMR (400 MHz, CDCl_3 , 328 K): $\delta = 7.31\text{--}7.25$ (m, 1H, CH_{dipp}), 7.20–7.14 (m, 2H, CH_{dipp}), 3.77 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.40 (sept., $^3J_{\text{HH}} = 6.8$ Hz, 1H, CH_{IPr}), 3.25 (sept., $^3J_{\text{HH}} = 6.8$ Hz, 1H, CH_{IPr}), 2.51 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 1.84–1.65 (m, 2H, CH_2), 1.52–1.36 (m, 3H, CH_2), 1.35–1.26 (m, 6H, $\text{CH}_3(\text{IPr})$), 1.31 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.28 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.25 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}_3(\text{IPr})$), 1.24 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}_3(\text{IPr})$), 1.06–1.01 (m, 1H, CH_2), 0.72 (br, 6H, SiCl- CH_3), 0.51 (s, 3H, Si- CH_3), 0.47 (s, 3H, Si- CH_3). ^{13}C NMR (101 MHz, CDCl_3 , 328 K): $\delta = 161.4$ (d, $^2J_{\text{CP}} = 26.0$ Hz, N-C), 148.4 (s, C_{dipp}), 147.4 (s, C_{dipp}), 142.1 (s, N- C_{dipp}), 127.5 (s, CH_{dipp}), 124.4 (s, CH_{dipp}), 124.2 (s, CH_{dipp}), 121.2 (d, $^1J_{\text{CP}} = 58.5$ Hz, C-P), 50.9 (d, $^2J_{\text{CP}} = 13.6$ Hz, C_{IBu}), 50.7 (d, $^2J_{\text{CP}} = 11.5$ Hz, C_{IBu}), 48.6 (d, $^2J_{\text{CP}} = 3.2$ Hz, $\text{CH}_{\text{bridgehead}}$), 46.7 (s, CH_2), 42.8 (s, $\text{CH}_{\text{bridgehead}}$), 32.6 (d, $^3J_{\text{CP}} = 4.6$ Hz, $\text{CH}_3(\text{Bu})$), 32.2 (d, $^3J_{\text{CP}} = 5.3$ Hz, $\text{CH}_3(\text{Bu})$), 28.2 (s, CH_2), 27.9 (s, CH_{IPr}), 27.7 (s, CH_{IPr}), 26.8 (s, CH_2), 25.5 (s, $\text{CH}_3(\text{IPr})$), 25.2 (s, $\text{CH}_3(\text{IPr})$), 24.9 (s, $\text{CH}_3(\text{IPr})$), 24.9 (s, $\text{CH}_3(\text{IPr})$), 8.0 (d, $^3J_{\text{CP}} = 5.3$ Hz, Si- CH_3), 6.3 (s, Si- CH_3), 6.1 (br d, $^2J_{\text{CP}} = 22.0$ Hz, 2 SiCl- CH_3). ^{31}P NMR (162 MHz, CDCl_3 , 328 K): $\delta = 114.0$ (br). ^{29}Si NMR (80 MHz, CDCl_3 , 328 K): $\delta = 10.3$ (br, SiMe_2Cl), 9.1 (s, SiMe_2).

Synthesis of 2c ($\text{R}^1 = \text{R}^2 = \text{Cl}$; $\text{R}^3 = \text{Me}$): To a solution of iminophosphine **1** ($\text{PR}_2 = \text{cyclic diaminophosphine}$) (2.00 g, 4.0 mmol) in THF (20 mL) was added dropwise at -80°C a solution of *n*-butyllithium 1.6 M in hexane (2.5 mL, 4.0 mmol) and stirred for 1 h. The crude was warmed up at room temperature and stirred for 1 h, then cooled to -80°C and trichloromethylsilane (0.47 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h, then the solvent was removed under vacuum. Product **2c** was extracted with heptane and colorless crystals were obtained from a saturated heptane solution at -30°C (1.76 g, 72 % yield). ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 7.33\text{--}7.27$ (m, 1H, CH_{dipp}), 7.20–7.14 (m, 2H, CH_{dipp}), 3.73 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 3.31 (sept., $^3J_{\text{HH}} = 6.7$ Hz, 1H, CH_{IPr}), 3.18 (sept., $^3J_{\text{HH}} = 6.8$ Hz, 1H, CH_{IPr}), 2.43 (s, 1H, $\text{CH}_{\text{bridgehead}}$), 1.80–1.63 (m, 2H, CH_2), 1.47–1.31 (m, 3H, CH_2), 1.28 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}_3(\text{IPr})$), 1.26 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.25–1.18 (m, 3 x 3H, $\text{CH}_3(\text{IPr})$ overlapped by $\text{CH}_3(\text{Bu})$), 1.23 (s, 9H, $\text{CH}_3(\text{Bu})$), 1.07 (br s, 3H, SiCl₂- CH_3), 1.03–1.00 (m, 1H, CH_2), 0.48 (s, 3H, Si- CH_3), 0.44 (s, 3H, Si- CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta = 159.6$ (d, $^2J_{\text{CP}} = 25.8$ Hz, N-C), 148.9 (s, C_{dipp}), 147.7 (s, C_{dipp}), 140.9 (s, N- C_{dipp}), 128.3 (s, CH_{dipp}), 124.7 (s, CH_{dipp}), 124.6 (s, CH_{dipp}), 123.8 (d, $^1J_{\text{CP}} = 56.5$ Hz, C-P), 51.1 (d, $^2J_{\text{CP}} = 13.4$ Hz, C_{IBu}), 50.9 (d, $^2J_{\text{CP}} = 11.6$ Hz, C_{IBu}), 48.6 (d, $^2J_{\text{CP}} = 2.9$ Hz, $\text{CH}_{\text{bridgehead}}$), 47.1 (s, CH_2), 43.1 (s, $\text{CH}_{\text{bridgehead}}$), 32.6 (d, $^3J_{\text{CP}} = 4.5$ Hz, $\text{CH}_3(\text{Bu})$), 32.2 (d, $^3J_{\text{CP}} = 5.1$ Hz, $\text{CH}_3(\text{Bu})$), 28.4 (s, 2 CH_{IPr}), 28.2 (s, CH_2), 28.1 (s, 2 CH_{IPr}), 26.9 (s, CH_2), 25.7 (s, $\text{CH}_3(\text{IPr})$), 25.3 (s, $\text{CH}_3(\text{IPr})$), 24.7 (s, $\text{CH}_3(\text{IPr})$), 24.6 (s, $\text{CH}_3(\text{IPr})$), 9.7 (d, $^2J_{\text{CP}} = 24.9$ Hz, SiCl- CH_3), 7.9 (d, $^3J_{\text{CP}} = 5.2$ Hz, Si- CH_3), 6.2 (s, Si- CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2): $\delta = 111.3$ (s). ^{29}Si NMR (99 MHz, CD_2Cl_2): $\delta = 10.1$ (s, SiMe_2), -5.5 (s, SiMeCl_2).

Synthesis of 2d ($\text{R}^1 = \text{R}^2 = \text{Cl}$; $\text{R}^3 = \text{H}$; $\text{PR}_2 = \text{cyclic diaminophosphine}$): Intense yellow solid (1.728 g, 72 %). Spectroscopic data are in perfect agreement with the values already reported.^{10a}

Synthesis of 2e ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Cl}$): Orange crystals (8.6 g, 66 %). Spectroscopic data are in perfect agreement with the values already reported.²²

Synthesis of 2f ($\text{R}^1 = \text{Cl}$; $\text{R}^2 = \text{R}^3 = \text{Me}$): To a solution of iminophosphine **1** ($\text{PR}_2 = \text{PPh}_2$) (1.01 g, 2.2 mmol) in THF (25 mL) was added dropwise at -80°C a solution of *n*-butyllithium 1.6 M in hexane (1.4 mL, 2.2 mmol) and stirred for 1 h. The reaction mixture is then warmed up to room temperature and stirred for 1 h, then cooled again to -80°C and dichlorodimethylsilane (0.27 mL, 2.2 mmol) was added

dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h before removal of the solvent under vacuum. Product **2f** was extracted with heptane and colourless crystals were obtained from a saturated heptane solution at -30 °C (1.11 g, 88 % yield). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.45-6.97 (m, 13H, P(C₆H₅)₂ + 3 CH_{dipp}), 3.70 (s, 1H, CH_{bridgehead}), 3.36-3.12 (br, 2H, CH_{iPr}), 3.06 (s, 1H, CH_{bridgehead}), 1.89-1.71 (m, 1H + 1H, CH₂), 1.60-1.42 (m, 2H, CH₂), 1.35-1.28 (m, 1H, CH₂), 1.25 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.15 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.04 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.82-0.20 (br, 6H + 1H, 2 Si-CH₃ + CH₂), 0.74 (d, ³J_{HH} = 6.9 Hz, 3H, CH_{3iPr}). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 165.0 (d, ²J_{CP} = 21.2 Hz, N-C), 148.8 (s, C_{dipp}), 148.7 (s, C_{dipp}), 146.2 (s, C_{dipp}), 146.2 (s, C_{dipp}), 143.7 (d, ¹J_{CP} = 12.5 Hz, P-C_{Ph}), 140.4 (d, ⁴J_{CP} = 3.6 Hz N-C_{dipp}), 138.6 (d, ¹J_{CP} = 17.4 Hz, P-C_{Ph}), 136.8 (d, ¹J_{CP} = 25.2 Hz, CH_{Ph}), 131.6 (d, ¹J_{CP} = 15.1 Hz, CH_{Ph}), 129.1 (s, CH_{Ph}), 128.2 (s, CH_{Ph}), 127.9 (d, ¹J_{CP} = 2.5 Hz, CH_{Ph}), 127.8 (d, ¹J_{CP} = 3.0 Hz, CH_{Ph}), 126.3 (s, CH_{dipp}), 125.4 (s, CH_{dipp}), 124.6 (s, CH_{dipp}), 107.2 (d, ¹J_{CP} = 21.5 Hz, C-P), 49.1 (d, ³J_{CP} = 5.5 Hz, CH_{bridgehead}), 47.2 (s, CH₂), 47.0 (d, ³J_{CP} = 5.2 Hz, CH_{bridgehead}), 28.5 (s, CH_{iPr}), 28.2 (s, CH_{iPr}), 27.7 (s, CH₂), 27.6 (s, CH₂), 25.9 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 24.9 (s, CH_{3iPr}), 24.6 (d, ¹J_{CP} = 5.8 Hz, CH_{3iPr}), 5.1 (br, Si-CH₃). ³¹P NMR (121 MHz, CD₂Cl₂): δ = -25.4. ²⁹Si NMR (60 MHz, CD₂Cl₂): δ = 11.5. M.p. = 101.1 °C.

Synthesis of 2g (R¹ = R² = Cl; R³ = Me): To a solution of iminophosphine **1** (PR₂ = PPh₂) (2.94 g, 6.5 mmol) in THF (25 mL) was added dropwise at -80 °C a solution of *n*-butyllithium 1.6 M in hexane (4.14 mL, 6.5 mmol) and stirred for 1 h. The reaction mixture is then warmed up to room temperature and stirred for 1 h, then cooled again to -80 °C and trichloromethylsilane (0.78 mL, 6.5 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1 h before removal of the solvent under vacuum. Product **2g** was extracted with heptane and pale-yellow crystals were obtained from a saturated heptane solution at -30 °C (2.48 g, 67 % yield). ¹H NMR (300 MHz, C₆D₆): δ = 7.43-6.90 (m, 13H, P(C₆H₅)₂) + 3 CH_{dipp}), 3.91 (s, 1H, CH_{bridgehead}), 3.42 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 3.28 (sept., ³J_{HH} = 6.9 Hz, 1H, CH_{iPr}), 3.08 (s, 1H, CH_{bridgehead}), 1.91-1.76 (m, 1H, CH₂), 1.75-1.50 (m, 2H, CH₂), 1.47, 1.45-1.30 (m, 1H, CH₂), 1.24 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.17 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.09 (d, ³J_{HH} = 6.9 Hz, 3H, CH_{3iPr}), 0.95-0.80 (m, 1H, CH₂), 0.78 (d, ³J_{HH} = 6.9 Hz, 3H, CH_{3iPr}), 0.44 (s, 3H, Si-CH₃). ¹³C NMR (75 MHz, C₆D₆): δ = 162.7 (d, ²J_{CP} = 20.7 Hz, N-C), 149.2 (d, ⁵J_{CP} = 6.2 Hz, C_{dipp}), 146.2 (d, ⁵J_{CP} = 2.2 Hz, C_{dipp}), 143.4 (d, ¹J_{CP} = 12.4 Hz, P-C_{Ph}), 138.9 (d, ⁴J_{CP} = 3.8 Hz C-N), 138.1 (d, ¹J_{CP} = 17.6 Hz, P-C_{Ph}), 136.9 (d, ¹J_{CP} = 25.4 Hz, CH_{Ph}), 131.7 (d, ¹J_{CP} = 15.1 Hz, CH_{Ph}), 129.3 (s, CH_{Ph}), 129.1 (s, CH_{Ph}), 128.0 (d, ¹J_{CP} = 6.1 Hz, CH_{Ph}) overlapped by deuterated solvent), 127.9 (d, ¹J_{CP} = 11.9 Hz, CH_{Ph} overlapped by deuterated solvent), 126.5 (s, CH_{dipp}), 125.4 (s, CH_{dipp}), 125.1 (s, CH_{dipp}), 111.1 (d, ¹J_{CP} = 24.0 Hz, C-P), 49.2 (d, ³J_{CP} = 4.9 Hz, CH_{bridgehead}), 47.4 (s, CH₂), 47.1 (d, ²J_{CP} = 5.1 Hz, CH_{bridgehead}), 28.7 (s, CH_{iPr}), 28.2 (s, CH_{iPr}), 27.5 (s, CH₂), 27.4 (s, CH₂), 26.0 (d, ¹J_{CP} = 6.2 Hz, CH_{3iPr}), 25.1 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 6.9 (s, Si-CH₃). ³¹P NMR (121 MHz, C₆D₆): δ = -26.1. ²⁹Si NMR (60 MHz, C₆D₆): δ = -5.0. M.p. = 94.3 °C.

Synthesis of 3: To a solution of **2a** (300 mg, 0.54 mmol) in dichloromethane (4 mL) was added trityl cation (496 mg, 0.54 mmol), and the reaction mixture turns red immediately. The solution was concentrated and cooled as quickly as possible to -30 °C, affording **3** as pink crystals (0.437 g, 55 % yield). The product is not stable in solution at room temperature, and therefore we applied low-temperature NMR (213 K) to characterise it. ¹H NMR (400 MHz, CD₂Cl₂, 213 K): δ = 7.44-7.09 (m, 13H, C(C₆H₅)₂ and CH_{dipp}), 6.95 (br, 2H, P-CH-CH=CH), 6.13 (br, 2H, P-CH-CH=CH), 5.20 (d, ²J_{PH} = 36.2 Hz, 1H, P-CH), 5.04 (br s, 1H, SiH), 3.79 (br, 1H, CH_{bridgehead}), 3.22 (br, 1H, CH_{iPr}), 3.06 (br, 1H, CH_{iPr}), 2.96 (br, 1H, CH_{bridgehead}), 2.07-1.61 (br(m), 3H, 2 CH₂), 1.57-0.97 (m, 15H, 4 CH_{3iPr} and 2 CH₂), 1.41 (s, 9H, CH_{3iBu}), 1.34 (s, 9H, CH_{3iBu}), 0.77 (s, 3H, Si-CH₃), 0.76 (s, 3H, Si-CH₃), 0.46 (s, 3H, SiH-CH₃), -0.10 (s, 3H, SiH-CH₃). ¹³C NMR (101 MHz, CD₂Cl₂, 213 K): δ = 174.0 (d, ²J_{CP} = 7.1 Hz, N-C), 147.8 (br d, ¹J_{CF} = 240.0 Hz, C_{Ar}-F), 147.0 (s, C_{dipp}), 145.8 (s, C_{dipp}), 143.4 (d, ¹J_{CP} = 12.7 Hz, C(Ph)₂), 140.7 (d, ¹J_{CP} = 4.4 Hz, C_{Ph}), 140.6 (d, ¹J_{CP} = 4.3 Hz, C_{Ph}), 138.7 (s, N-C_{dipp}), 138.2 (br d, ¹J_{CF} = 245.7 Hz, C_{Ar}-F), 136.1 (br d, ¹J_{CF} = 245.1 Hz, C_{Ar}-F), 131.9 (d, ³J_{CP} = 16.3 Hz, P-CH-CH=CH), 131.7 (d, ³J_{CP} = 14.1 Hz, P-CH-CH=CH), 130.8 (s, CH_{Ph} and CH_{dipp}), 128.3 (CH_{Ph}), 128.2

(CH_{Ph}), 125.8 (d, ¹J_{CP} = 12.5 Hz, C=C(Ph)₂), 125.6 (s, CH_{dipp}), 125.5 (s, CH_{dipp}), 123.7 (br, B-C_{Ar}), 120.9 (br, P-CH-CH=CH), 119.4 (br, P-CH-CH=CH), 101.9 (d, ¹J_{CP} = 89.7 Hz, C-P), 53.5 (d, C_{iBu} overlapped by deuterated solvent), 53.4 (d, C_{iBu} overlapped by deuterated solvent), 51.9 (d, ²J_{CP} = 11.6 Hz, CH_{bridgehead}), 49.1 (d, ²J_{CP} = 8.6 Hz, CH_{bridgehead}), 47.3 (d, ²J_{CP} = 61.5 Hz, P-CH), 43.8 (s, CH₂), 32.3 (d, 2 CH_{3iBu} overlapped), 28.4 (s, CH_{iPr}), 28.0 (s, CH₂), 27.9 (s, CH_{iPr}), 26.9 (s, CH₂), 25.3 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 24.9 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 4.7 (s, Si-CH₃), 3.6 (d, ³J_{CP} = 2.9 Hz, Si-CH₃), 2.8 (s, SiH-CH₃), -3.4 (s, SiH-CH₃). ³¹P NMR (162 MHz, CD₂Cl₂, 213 K): δ = 49.3 (s). ¹⁹F NMR (376 MHz, CD₂Cl₂): δ = -132.8 (br, C_{Ar}-F_{ortho}), -163.5 (t, ¹J_{FF} = 20.4 Hz, C_{Ar}-F_{para}), -167.3 (t, ¹J_{FF} = 18.0 Hz, C_{Ar}-F_{meta}). ¹¹B NMR (128 MHz, CD₂Cl₂, 213 K): δ = -16.9 (s, B_{Ar}). ²⁹Si NMR (80 MHz, CD₂Cl₂, 213 K): δ = 22.3 (d, ²J_{SIP} = 4.5 Hz, SiMe₂), -3.7 (s, SiMe₂H).

Synthesis of 4b (R² = R³ = Me): To a solution of **2b** (300 mg, 0.50 mmol) in dichloromethane (3 mL) was added potassium tetrakis(pentafluorophenyl)borane (0.360, 0.50 mmol). After stirring for 10 min, the solution was filtered then the solvents are removed under vacuum to give **4b** as a white powder (0.490 g, 79 %). Crystals suitable for X-Ray diffraction analysis were obtained from a concentrated dichloromethane solution. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.45-7.24 (m, 3H, CH_{dipp}), 3.39 (s, 1H, CH_{bridgehead}), 2.96 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 2.83 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 2.71 (s, 1H, CH_{bridgehead}), 2.06-1.83 (m, 2H, CH₂), 1.81-1.66 (m, 2H, CH₂), 1.61-1.52 (m, 2H, CH₂), 1.40 (s, 9H, CH_{3iBu}), 1.37 (s, 9H, CH_{3iBu}), 1.29 (d, ³J_{HH} = 4.0 Hz, 3H, CH_{3iPr}), 1.26 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.18 (d, ³J_{HH} = 4.0 Hz, 3H, CH_{3iPr}), 1.16 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 0.82 (d, ³J_{HP} = 6.6 Hz, 3H, Si⁺-CH₃), 0.77 (s, 3H, Si-CH₃), 0.69 (d, ³J_{HP} = 6.4 Hz, 3H, Si⁺-CH₃), 0.65 (s, 3H, Si-CH₃). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 192.3 (d, ²J_{CP} = 25.9 Hz, N-C), 148.6 (br d, ¹J_{CF} = 241.3 Hz, C_{Ar}-F), 147.5 (s, C_{dipp}), 147.3 (s, C_{dipp}), 138.6 (br d, ¹J_{CF} = 244.8 Hz, C_{Ar}-F), 136.7 (br d, ¹J_{CF} = 245.8 Hz, C_{Ar}-F), 132.1 (d, ³J_{CP} = 3.1 Hz, N-C_{dipp}), 129.9 (s, CH_{dipp}), 125.8 (s, CH_{dipp}), 125.7 (s, CH_{dipp}), 99.0 (d, ¹J_{CP} = 68.9 Hz, C-P), 53.3 (d, ²J_{CP} = 21.2 Hz, C_{iBu}), 53.2 (d, ²J_{CP} = 19.4 Hz, C_{iBu}), 48.7 (d, ³J_{CP} = 6.0 Hz, CH₂), 45.0 (d, ²J_{CP} = 10.5 Hz, CH_{bridgehead}), 41.5 (s, CH_{bridgehead}), 32.9 (d, ³J_{CP} = 5.6 Hz, CH_{3iBu}), 32.6 (d, ³J_{CP} = 5.6 Hz, CH_{3iBu}), 28.5 (s, CH_{iPr}), 28.4 (d, ³J_{CP} = 5.6 Hz, CH_{3iPr}), 28.1 (s, CH₂), 26.1 (s, CH_{3iPr}), 25.7 (d, ³J_{CP} = 1.8 Hz, CH₂), 25.3 (s, CH_{3iPr}), 24.5 (s, CH_{3iPr}), 24.4 (s, CH_{3iPr}), 6.1 (s, Si-CH₃), 4.3 (d, ³J_{CP} = 1.8 Hz, Si-CH₃), 1.4 (d, ²J_{CP} = 14.2 Hz, Si⁺-CH₃), 0.7 (d, ²J_{CP} = 13.4 Hz, Si⁺-CH₃). C_{iPr} attached to boron atom could not be detected. ³¹P NMR (121 MHz, CD₂Cl₂): δ = 39.6 (¹J_{PSi} = 132 Hz). ¹¹B NMR (96 MHz, CD₂Cl₂): δ = -16.6 (s, B_{Ar}). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar}-F_{ortho}), -163.7 (t, ¹J_{FF} = 20.3 Hz, C_{Ar}-F_{para}), -167.5 (t, ¹J_{FF} = 18.3 Hz, C_{Ar}-F_{meta}). ²⁹Si NMR (60 MHz, CD₂Cl₂): δ = 21.4 (d, ²J_{SIP} = 2.9 Hz, SiMe₂), 6.1 (d, ¹J_{SIP} = 132.0 Hz, Si⁺). Elemental Analysis: Calc. for C₅₅H₅₅BF₂₀N₃PSi₂: C, 53.45; H, 4.49; N, 3.40. Found: C, 53.21; H, 4.43; N, 3.38. M.p. = 86.1 °C.

Synthesis of 4c (R² = Me, R³ = Cl): White powder (0.504 g, 82 %). Crystals suitable for X-Ray diffraction analysis were obtained from a concentrated dichloromethane solution. A 50-50 diastereomer mixture is obtained. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.47-7.40 (m, 2H, CH_{dipp}), 7.35-7.26 (m, 4H, CH_{dipp}), 3.43 (s, 2H, CH_{bridgehead}), 3.07 (sept., ³J_{HH} = 6.6 Hz, 1H, CH_{iPr}), 2.91 (sept., ³J_{HH} = 6.9 Hz, 1H, CH_{iPr} overlapped with CH_{iPr}), 2.89 (sept., ³J_{HH} = 6.9 Hz, 1H, CH_{iPr} overlapped with CH_{iPr}), 2.83-2.70 (br, 1H, CH_{iPr} overlapped by CH_{bridgehead}), 2.83-2.70 (br, 2H, CH_{bridgehead} overlapped by CH_{iPr}), 2.05-1.89 (m, 4H, CH₂), 1.81-1.66 (m, 4H, CH₂), 1.64-1.56 (m, 2H, CH₂), 1.45 (d, ⁴J_{PH} = 0.88 Hz, 9H, CH_{3iBu}), 1.44 (d, ⁴J_{PH} = 0.87 Hz, 3H, CH_{3iBu}), 1.40 (d, ⁴J_{PH} = 0.98 Hz, 3H, CH_{3iBu}), 1.40-1.36 (m, 2H, CH₂), 1.38 (d, ⁴J_{PH} = 0.94 Hz, 3H, CH_{3iBu}), 1.32-1.26 (m, 12H, CH_{3iPr}), 1.21-1.14 (m, 12H, CH_{3iPr} overlapped by Si⁺-CH₃), 1.21-1.14 (d, ³J_{PH} = 4.1 Hz*, 3H, Si⁺-CH₃ overlapped by CH_{3iPr}), 1.03 (d, ³J_{PH} = 4.1 Hz, 3H, Si⁺-CH₃), 0.81 (d, ²J_{PH} = 2.2 Hz, 6H, Si-CH₃), 0.70 (d, ²J_{PH} = 2.5 Hz, 6H, Si-CH₃). * coupling constant determined by HSQC. ²⁹Si NMR (101 MHz, CD₂Cl₂): δ = 192.4 (d, ²J_{CP} = 23.2 Hz, N-C), 192.3 (d, ²J_{CP} = 23.2 Hz, N-C), 148.6 (br d, ¹J_{CF} = 240.4 Hz, C_{Ar}-F), 148.1 (s, C_{dipp}), 147.9 (s, C_{dipp}), 147.0 (s, C_{dipp}), 146.7 (s, C_{dipp}), 138.6 (br d, ¹J_{CF} = 245.1 Hz, C_{Ar}-F), 136.7 (br d, ¹J_{CF} = 246.4 Hz, C_{Ar}-F), 130.7 (d, ³J_{CP} = 2.8 Hz, N-C_{dipp}), 130.6 (d, ³J_{CP} = 2.6 Hz, N-C_{dipp}), 130.4 (s, CH_{dipp}), 130.3 (s, CH_{dipp}), 126.3 (s, CH_{dipp}), 126.2 (s, CH_{dipp}), 125.8 (s, CH_{dipp}), 125.7 (s, CH_{dipp}), 124.4 (broad s, B-C_{Ar}), 99.3 (d, ¹J_{CP} = 74.6 Hz, C-P), 99.2 (d, ¹J_{CP} =

72.8 Hz, C-P), 54.4 (d, C_{IBu} overlapped by deuterated solvent), 54.2 (d, ²J_{CP} = 1.5 Hz, C_{IBu}), 53.7 (d, ²J_{CP} = 1.2 Hz, C_{IBu}), 53.5 (d, ²J_{CP} = 1.2 Hz, C_{IBu}), 48.9 (d, ³J_{CP} = 6.7 Hz, CH₂), 48.4 (d, ³J_{CP} = 6.1 Hz, CH₂), 45.3 (s, CH_{bridgehead}), 45.2 (s, CH_{bridgehead}), 41.8 (s, CH_{bridgehead}), 41.6 (s, CH_{bridgehead}), 32.8 (d, ³J_{CP} = 5.6 Hz, 2 CH_{3IBu}), 32.5 (d, ³J_{CP} = 5.8 Hz, CH_{3IBu}), 32.4 (d, ³J_{CP} = 5.6 Hz, CH_{3IBu}), 28.8 (s, CH_{IPr}), 28.7 (s, CH_{IPr}), 28.6 (s, CH_{IPr}), 28.5 (s, CH_{IPr}), 27.9 (s, CH₂), 27.6 (s, CH₂), 26.1 (s, CH_{3IPr}), 25.7 (s, CH_{3IPr}), 25.5 (d, ³J_{CP} = 1.8 Hz, CH₂), 25.5 (d, ³J_{CP} = 1.8 Hz, CH₂), 25.3 (s, CH_{3IPr}), 25.1 (s, CH_{3IPr}), 25.0 (s, CH_{3IPr}), 24.9 (s, CH_{3IPr}), 24.4 (s, CH_{3IPr}), 24.3 (s, CH_{3IPr}), 6.0 (s, Si-CH₃), 5.9 (s, 2 Si-CH₃), 4.4 (d, ²J_{CP} = 18.9 Hz, Si⁺-CH₃), 4.3 (d, ³J_{CP} = 1.7 Hz, Si-CH₃), 4.2 (d, ³J_{CP} = 1.7 Hz, Si-CH₃), 3.7 (d, ²J_{CP} = 18.0 Hz, Si⁺-CH₃). ³¹P NMR (162 MHz, CD₂Cl₂): δ = 30.2 (¹J_{PSi} = 172.6 Hz), 30.0 (¹J_{PSi} = 171.2 Hz). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -132.5 (br, C_{Ar-Fortho}), -163.3 (t, J_{FF} = 20.5 Hz, C_{Ar-Fpara}), -167.0 (t, J_{FF} = 19.3 Hz, C_{Ar-Fmeta}). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 23.8 (d, ²J_{SIP} = 2.5 Hz, SiMe₂), 23.8 (d, ²J_{SIP} = 2.7 Hz, SiMe₂), -0.3 (d, ¹J_{SIP} = 172.6 Hz, Si⁺), -2.1 (d, ¹J_{SIP} = 171.2 Hz, Si⁺). M.p. = 157.7 °C.

Synthesis of 4d (R² = Cl, R³ = H): White powder (0.511 g, 82 %). Crystals suitable for X-Ray diffraction analysis were obtained from a concentrated chloroform solution. A single diastereomer is obtained. ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.43 (m, 1H, CH_{dipp}), 7.33-7.28 (m, 2H, CH_{dipp}), 5.90 (d, 1H, ²J_{PH} = 58.4 Hz, SiH), 3.45 (s, 1H, CH_{bridgehead}), 2.96 (sept., ³J_{HH} = 6.9 Hz, 1H, CH_{IPr}), 2.87 (sept., ³J_{HH} = 6.9 Hz, 1H, CH_{IPr} overlapped by CH_{bridgehead}), 2.83 (s, 1H, CH_{bridgehead} overlapped by CH_{IPr}), 2.07-1.93 (m, 2H, CH₂), 1.82-1.60 (m, 4H, 2 CH₂), 1.43 (d, 9H, ⁴J_{PH} = 0.8 Hz, CH_{3IBu}), 1.41 (d, 9H, ⁴J_{PH} = 0.8 Hz, CH_{3IBu}), 1.29 (d, 3H, ³J_{HH} = 6.8 Hz, CH_{3IPr}), 1.27 (d, 3H, ³J_{HH} = 6.8 Hz, CH_{3IPr}), 1.24 (d, 6H, ³J_{HH} = 6.8 Hz, 2 CH_{3IPr}), 0.80 (s, 3H, SiMe₂), 0.72 (s, 3H, SiMe₂). ¹³C NMR (101 MHz, CDCl₃): δ = 192.3 (d, ²J_{CP} = 22.2 Hz, N-C), 148.2 (br d, J_{CF} = 241.3 Hz, C_{Ar-F}), 146.7 (s, C_{dipp}), 146.6 (s, C_{dipp}), 138.3 (br d, J_{CF} = 244.9 Hz, C_{Ar-F}), 136.2 (br d, J_{CF} = 244.1 Hz, C_{Ar-F}), 130.4 (s, CH_{dipp}), 130.1 (s, N-C_{dipp}), 125.6 (s, 2 CH_{dipp}), 100.3 (d, ¹J_{CP} = 76.7 Hz, C-P), 53.5 (br, C_{IBu}), 53.4 (br, C_{IBu}), 48.3 (d, J_{CP} = 6.4 Hz, CH₂), 44.8 (d, ³J_{CP} = 10.0 Hz, CH_{bridgehead}), 41.6 (s, CH_{bridgehead}), 32.6 (d, ³J_{CP} = 5.8 Hz, CH_{3IBu}), 32.4 (d, ³J_{CP} = 5.8 Hz, CH_{3IBu}), 28.8 (s, CH_{IPr}), 28.6 (s, CH_{IPr}), 27.6 (s, CH₂), 25.1 (s, CH_{3IPr}), 24.8 (d, J_{CP} = 1.7 Hz, CH₂), 24.7 (s, CH_{3IPr}), 24.5 (s, CH_{3IPr}), 24.2 (s, CH_{3IPr}), 5.1 (s, SiMe₂), 3.9 (d, ³J_{CP} = 1.7 Hz, SiMe₂). C_{ipso} attached to boron atom could not be detected. ³¹P NMR (162 MHz, CDCl₃): δ = 28.2 (¹J_{SIP} = 169.1 Hz, ²J_{PH} = 58.5 Hz). ¹¹B NMR (160 MHz, CDCl₃): δ = -16.6 (s, BAr). ¹⁹F NMR (471 MHz, CDCl₃): δ = -132.5 (br, C_{Ar-Fortho}), -163.3 (t, J_{FF} = 20.5 Hz, C_{Ar-Fpara}), -167.0 (t, J_{FF} = 19.3 Hz, C_{Ar-Fmeta}). ²⁹Si NMR (60 MHz, CDCl₃): δ = 24.0 (s, SiMe₂), -23.3 (d, ¹J_{SIP} = 169.1 Hz, Si⁺). M.p. = 150.3 °C.

Synthesis of 4e (R² = R³ = Cl): White powder (0.466 g, 77 %). Crystals suitable for X-Ray diffraction analysis were obtained from a concentrated chloroform solution. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.54-7.24 (m, 3H, CH_{dipp}), 3.48 (s, 1H, CH_{bridgehead}), 3.01 (sept., ³J_{HH} = 6.8 Hz, 1H, CH_{IPr}), 2.93-2.77 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{IPr} overlapped by CH_{bridgehead}), 2.88-2.77 (s, 1H, CH_{bridgehead} overlapped by CH_{IPr}), 2.12-1.55 (m, 2H, CH₂), 2.12-1.55 (m, 2H, CH₂), 1.46 (s, 9H, CH_{3IBu}), 1.45 (s, 9H, CH_{3IBu}), 1.33 (d, 3H, ³J_{HH} = 5.5 Hz, CH_{3IPr}), 1.31 (d, 3H, ³J_{HH} = 5.5 Hz, CH_{3IPr}), 0.80 (d, 6H, ³J_{HH} = 6.7 Hz, CH_{3IPr}), 0.85 (s, 3H, SiMe₂), 0.75 (s, 3H, SiMe₂). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 191.7 (d, ²J_{CP} = 20.2 Hz, N-C), 148.0 (br d, J_{CF} = 243.6 Hz, C_{Ar-F}), 147.2 (s, C_{dipp}), 146.9 (s, C_{dipp}), 138.3 (br d, J_{CF} = 245.5 Hz, C_{Ar-F}), 136.3 (br d, J_{CF} = 247.4 Hz, C_{Ar-F}), 130.3 (s, CH_{dipp}), 129.0 (br, N-C_{dipp}), 125.8 (s, CH_{dipp}), 125.7 (s, CH_{dipp}), 98.6 (d, ¹J_{CP} = 80.1 Hz, C-P), 54.3 (d, ³J_{CP} = 1.9 Hz, C_{IBu}), 54.1 (d, C_{IBu} overlapped by deuterated solvent), 47.9 (d, J_{CP} = 6.8 Hz, CH₂), 45.3 (d, ²J_{CP} = 9.6 Hz, CH_{bridgehead}), 41.6 (d, ³J_{CP} = 1.2 Hz, CH_{bridgehead}), 32.4 (d, ³J_{CP} = 5.9 Hz, CH_{3IBu}), 31.9 (d, ³J_{CP} = 5.9 Hz, CH_{3IBu}), 28.4 (s, CH_{IPr}), 28.3 (s, CH_{IPr}), 27.1 (s, CH₂), 25.3 (s, CH_{3IPr}), 24.9 (d, J_{CP} = 1.9 Hz, CH₂), 24.6 (s, CH_{3IPr}), 24.4 (s, CH_{3IPr}), 24.3 (s, CH_{3IPr}), 5.3 (s, SiMe₂), 3.7 (d, ³J_{CP} = 1.4 Hz, SiMe₂). C_{ipso} attached to boron atom could not be detected. ³¹P NMR (121 MHz, CD₂Cl₂): δ = 21.8 (¹J_{SIP} = 237.4 Hz). ¹¹B NMR (96 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar-Fortho}), -163.7 (t, J_{FF} = 20.3 Hz, C_{Ar-Fpara}), -167.5 (t, J_{FF} = 18.3 Hz, C_{Ar-Fmeta}). ²⁹Si NMR (60 MHz, CD₂Cl₂): δ =

25.6 (d, ²J_{SIP} = 2.88 Hz, SiMe₂), -21.6 (d, ¹J_{SIP} = 237.4 Hz, Si⁺). Elemental Analysis: Calc. for C₅₃H₄₉BCl₂F₂₀N₃PSi₂: C, 49.86; H, 3.87; N, 3.29. Found: C, 49.79; H, 3.83; N, 3.35. M.p. = 189.4 °C.

Synthesis of 5f (R² = R³ = Me): To a solution of **2f** (136 mg, 0.25 mmol) in dichloromethane (2 mL) was added potassium tetrakis(pentafluorophenyl)borane (179 mg, 0.25 mmol). After stirring for 10 min, the solution was filtered and all the volatiles are removed under vacuum to give **5f** as a white powder (213 mg, 72 %). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.83-7.56 (m, 10H, P(C₆H₅)₂), 7.45-7.20 (m, 3H, CH_{dipp}), 3.55 (s, 1H, CH_{bridgehead}), 3.06 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{IPr}), 2.79 (s, 1H, CH_{bridgehead}), 2.66 (sept., ³J_{HH} = 6.8 Hz, 1H, CH_{IPr}), 2.10-1.91 (m, 2 + 1H, CH₂), 1.67-1.58 (m, 1H, CH₂), 1.53-1.41 (m, 2H, CH₂), 1.28 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.26 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.14 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3IPr}), 1.06 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3IPr}), 0.81 (d, ³J_{PH} = 6.6 Hz, 3H, Si-CH₃), 0.51 (d, ³J_{PH} = 6.6 Hz, 3H, Si-CH₃). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 187.5 (d, ²J_{CP} = 16.4 Hz, N-C), 148.7 (br d, J_{CF} = 241.3 Hz, C_{Ar-F}), 148.0 (s, C_{dipp}), 147.9 (s, C_{dipp}), 138.8 (br d, J_{CF} = 244.6 Hz, C_{Ar-F}), 136.7 (br d, J_{CF} = 247.3 Hz, C_{Ar-F}), 134.5 (d, J_{CP} = 3.4 Hz, CH_{Ph}), 134.4 (d, J_{CP} = 3.4 Hz, CH_{Ph}), 133.2 (d, J_{CP} = 11.2 Hz, CH_{Ph}), 132.4 (d, J_{CP} = 11.3 Hz, CH_{Ph}), 131.6 (d, J_{CP} = 2.2 Hz, N-C_{dipp}), 131.0 (d, J_{CP} = 12.5 Hz, CH_{Ph}), 130.9 (d, J_{CP} = 12.7 Hz, CH_{Ph}), 130.0 (s, CH_{dipp}), 125.8 (s, CH_{dipp}), 125.7 (s, CH_{dipp}), 121.7 (d, ¹J_{CP} = 70.3 Hz, P-C_{Ph}), 119.5 (d, ¹J_{CP} = 74.0 Hz, P-C_{Ph}), 86.7 (d, ¹J_{CP} = 73.2 Hz, C-P), 49.3 (d, ³J_{CP} = 5.0 Hz, CH₂), 45.1 (d, ²J_{CP} = 8.9 Hz, CH_{bridgehead}), 42.8 (d, ³J_{CP} = 1.0 Hz, CH_{bridgehead}), 29.1 (s, CH₂), 28.7 (s, CH_{IPr}), 28.6 (s, CH_{IPr}), 26.4 (d, ³J_{CP} = 2.1 Hz, CH₂), 25.6 (s, CH_{3IPr}), 25.4 (s, CH_{3IPr}), 24.9 (s, CH_{3IPr}), 23.6 (s, CH_{3IPr}), -0.33 (d, ²J_{CP} = 15.0 Hz, Si⁺-CH₃), -3.0 (d, ²J_{CP} = 11.0 Hz, Si⁺-CH₃). C_{ipso} attached to boron atom could not be detected. ³¹P NMR (121 MHz, CD₂Cl₂): δ = -20.8 (¹J_{PSi} = 82.1 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = -132.9 (br, C_{Ar-Fortho}), -163.6 (t, J_{FF} = 20.4 Hz, C_{Ar-Fpara}), -167.4 (t, J_{FF} = 18.1 Hz, C_{Ar-Fmeta}). ¹¹B NMR (96 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (60 MHz, CD₂Cl₂): δ = 27.2 (d, ¹J_{PSi} = 82.1 Hz). M.p. = 84.6 °C.

Synthesis of 5g (R² = Cl; R³ = Me): To a solution of **2g** (300 mg, 0.53 mmol) in dichloromethane (2 mL) was added potassium tetrakis(pentafluorophenyl)borane (380 mg, 0.53 mmol). After stirring for 10 min, the solution was filtered by cannula and evaporated under vacuum to give **5g** as a white powder (484 mg, 76 %). Major isomer (76 %): ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.89-7.60 (m, 10H, P(C₆H₅)₂), 7.48-7.39 (m, 1H, CH_{dipp}), 7.37-7.29 (m, 1H, CH_{dipp}), 7.24-7.19 (m, 1H, CH_{dipp}), 3.58 (s, 1H, CH_{bridgehead}), 3.28 (sept., ³J_{HH} = 6.8 Hz, 1H, CH_{IPr}), 2.83 (s, 1H, CH_{bridgehead}), 2.46 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{IPr}), 2.11-1.91 (m, 2H, CH₂), 1.68-1.34 (m, 4H, 2 CH₂), 1.28 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.27 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.08 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3IPr}), 0.94 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3IPr}), 0.83 (d, ³J_{PH} = 4.3 Hz, 3H, Si-CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 185.9 (d, ²J_{CP} = 13.1 Hz, N-C), 148.6 (br d, J_{CF} = 241.7 Hz, C_{Ar-F}), 148.4 (s, C_{dipp}), 147.5 (s, C_{dipp}), 138.7 (br d, J_{CF} = 243.8 Hz, C_{Ar-F}), 136.7 (br d, J_{CF} = 243.8 Hz, C_{Ar-F}), 135.4 (d, J_{CP} = 3.4 Hz, CH_{Ph}), 135.2 (d, J_{CP} = 3.5 Hz, CH_{Ph}), 134.0 (d, J_{CP} = 11.1 Hz, CH_{Ph}), 132.6 (d, J_{CP} = 11.4 Hz, CH_{Ph}), 131.5 (d, J_{CP} = 12.8 Hz, CH_{Ph}), 130.9 (d, J_{CP} = 13.3 Hz, CH_{Ph}), 130.5 (s, CH_{dipp}), 126.2 (s, CH_{dipp}), 125.6 (s, CH_{dipp}), 124.5 (br, B-C_{Ar}), 119.5 (d, ¹J_{CP} = 72.5 Hz, P-C_{Ph}), 116.4 (d, ¹J_{CP} = 77.5 Hz, P-C_{Ph}), 89.2 (d, ¹J_{CP} = 74.6 Hz, C-P), 49.1 (d, ³J_{CP} = 5.5 Hz, CH₂), 45.4 (d, ²J_{CP} = 8.5 Hz, CH_{bridgehead}), 43.1 (d, ³J_{CP} = 1.8 Hz, CH_{bridgehead}), 29.0 (s, 2 CH_{IPr}), 28.8 (s, CH₂), 26.1 (d, ³J_C = 2.3 Hz, CH₂), 25.5 (s, CH_{3IPr}), 25.5 (s, CH_{3IPr}), 24.8 (s, CH_{3IPr}), 23.1 (s, CH_{3IPr}), 0.0 (d, ²J_{CP} = 15.1 Hz, Si⁺-CH₃). C_{ipso} attached to boron atom could not be detected. ³¹P NMR (202 MHz, CD₂Cl₂): δ = -24.3 (¹J_{PSi} = 124.6 Hz). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar-Fortho}), -163.6 (t, J_{FF} = 20.4 Hz, C_{Ar-Fpara}), -167.4 (t, J_{FF} = 18.1 Hz, C_{Ar-Fmeta}). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 15.4 (d, ¹J_{PSi} = 124.6 Hz). M.p. = 78.8 °C. Minor isomer (24 %): ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.89-7.59 (m, 10H, P(C₆H₅)₂*), 7.48-7.39 (m, 1H, CH_{dipp}*), 7.37-7.29 (m, 1H, CH_{dipp}*), 7.24-7.19 (m, 1H, CH_{dipp}*), 3.58 (s, 1H, CH_{bridgehead}*), 2.98 (sept., ³J_{HH} = 6.7 Hz, 1H, CH_{IPr}), 2.89-2.79 (br, 1H, CH_{IPr}*), 2.89-2.79 (br, 1H, CH_{bridgehead}*), 2.11-1.91 (m, 2H, CH₂*), 1.68-1.34 (m, 4H, 2 CH₂*), 1.31 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.26 (d, 3H, CH_{3IPr}*), 1.20 (d, ³J_{HH} = 6.7 Hz, 3H, CH_{3IPr}), 1.18 (d, ³J_{PH} = 4.4 Hz, 3H, Si-CH₃ overlapped with CH_{3IPr}), 1.17 (d, ³J_{HH} = 7.0 Hz, 3H, CH_{3IPr} overlapped with Si-CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ =

= 187.3 (d, J_{CP} = 13.9 Hz, N-C), 148.7 (br d, J_{CF} = 241.7 Hz, C_{Ar}-F), 148.6 (s, C_{dipp}), 147.5 (s, C_{dipp}*), 138.7 (br d, J_{CF} = 243.8 Hz, C_{Ar}-F), 136.7 (br d, J_{CF} = 243.8 Hz, C_{Ar}-F), 135.3 (d, J_{CP} = 3.5 Hz, CH_{Ph}), 135.1 (d, J_{CP} = 3.4 Hz, CH_{Ph}), 133.3 (d, J_{CP} = 11.3 Hz, CH_{Ph}), 133.1 (d, J_{CP} = 11.3 Hz, CH_{Ph}), 131.4 (d, CH_{Ph}*), 131.0 (d, CH_{Ph}*), 129.9 (s, CH_{dipp}), 126.2 (s, CH_{dipp}), 125.8 (s, CH_{dipp}), 124.5 (br, B-C_{Ar}), 118.8 (d, J_{CP} = 76.4 Hz, P-C_{Ph}), 118.3 (d, J_{CP} = 75.2 Hz, P-C_{Ph}), 87.0 (d, J_{CP} = 73.7 Hz, C-P), 49.1 (d, CH₂*), 45.5 (d, J_{CP} = 8.8 Hz, CH_{bridgehead}), 42.8 (s, CH_{bridgehead}), 28.9 (s, 2 CH_{iPr}), 28.5 (s, CH₂), 26.5 (d, J_C = 2.5 Hz, CH₂), 25.8 (s, CH_{3iPr}), 25.3 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 24.4 (s, CH_{3iPr}), 2.9 (d, J_{CP} = 17.8 Hz, Si⁺-CH₃). ³¹P NMR (202 MHz, CD₂Cl₂): δ = -24.1 (J_{PSi} = 117.4). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -132.9 (br, C_{Ar}-F_{ortho}), -163.6 (t, J_{FF} = 20.4 Hz, C_{Ar}-F_{para}), -167.4 (t, J_{FF} = 18.1 Hz, C_{Ar}-F_{meta}). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 15.3 (d, J_{PSi} = 117.4 Hz). All signals marked with * are overlapped by signals of the major isomer.

Synthesis of 6: In a J. Young NMR tube, to a solution of **5f** (50.0 mg, 0.042 mmol) in dichloromethane (0.3 mL) was added methyl acrylate (3.78 μL, 0.042 mmol) then the solution is warmed up at 50 °C for 4 hours. Then solution was evaporated under vacuum and the resulting crude was washed with 3 x 0.3 mL of pentane. Product **6** was isolated as a white powder in 60 % yield (32 mg). ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.83-7.53 (m, 8H, P(C₆H₅)₂), 7.43-7.36 (m, 1H, CH_{dipp}), 7.32-7.25 (m, 2H, CH_{dipp} overlapped by P(C₆H₅)₂), 7.32-7.25 (m, 2H, P(C₆H₅)₂ overlapped by CH_{dipp}), 3.94 (ddd, 1H, J_{PH} = 25.3 Hz, J_{HH} = 6.2 Hz, J_{HH} = 3.2 Hz, CH=C), 3.78 (ddd, 1H, J_{HH} = 17.7 Hz, J_{PH} = 14.3 Hz, J_{HH} = 3.2 Hz, P-CH₂), 3.52 (ddd, 1H, J_{HH} = 17.7 Hz, J_{PH} = 14.3 Hz, J_{HH} = 6.2 Hz, P-CH₂), 3.44 (s, 3H, O-CH₃), 3.41 (sept., J_{HH} = 6.9 Hz, 1H, CH_{iPr}), 3.11 (sept., J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 2.93 (br, 1H, CH_{bridgehead}), 2.49 (br, 1H, CH_{bridgehead}), 1.99-1.90 (m, 1H, CH₂), 1.80-1.52 (m, 3H, CH₂), 1.48-1.41 (m, 1H, CH₂), 1.38 (d, J_{PH} = 6.9 Hz, 3H, CH_{3iPr}), 1.31 (d, J_{PH} = 6.8 Hz, 3H, CH_{3iPr}), 1.27 (d, J_{PH} = 6.9 Hz, 3H, CH_{3iPr}), 1.24 (d, J_{PH} = 6.8 Hz, 3H, CH_{3iPr}), 1.11-1.07 (m, 1H, CH₂), 0.40 (s, 3H, Si-CH₃), -0.04 (s, Si-CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 177.6 (d, J_{CP} = 2.9 Hz, N-C), 156.9 (d, J_{CP} = 5.5 Hz, CH=C-O), 148.5 (br d, J_{CF} = 243.7 Hz, C_{Ar}-F), 147.6 (s, C_{dipp}), 146.7 (s, C_{dipp}), 138.6 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 137.4 (s, C_{dipp}), 136.6 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 134.3 (d, J_{CP} = 3.1 Hz, CH_{Ph}), 133.9 (d, J_{CP} = 2.8 Hz, CH_{Ph}), 131.9 (d, J_{CP} = 10.2 Hz, CH_{Ph}), 131.3 (d, J_{CP} = 8.7 Hz, CH_{Ph}), 130.3 (d, J_{CP} = 11.9 Hz, CH_{Ph}), 130.1 (d, J_{CP} = 13.0 Hz, CH_{Ph}), 129.5 (s, CH_{dipp}), 128.6 (d, J_{CP} = 91.3 Hz, P-C_{Ph}), 125.9 (s, CH_{dipp}), 125.6 (s, CH_{dipp}), 123.7 (d, J_{CP} = 89.6 Hz, P-C_{Ph}), 92.2 (d, J_{CP} = 73.2 Hz, C-P), 67.8 (d, J_{CP} = 10.6 Hz, CH=C), 56.0 (s, O-CH₃), 52.1 (d, J_{CP} = 12.9 Hz, CH_{bridgehead}), 49.9 (d, J_{CP} = 10.7 Hz, CH_{bridgehead}), 46.9 (d, J_{CP} = 5.8 Hz, CH₂), 28.8 (s, CH_{iPr}), 28.5 (s, CH₂), 28.4 (s, CH_{iPr}), 28.3 (d, J_{CP} = 58.2 Hz, P-CH₂), 26.2 (d, J_{CP} = 2.8 Hz, CH₂), 25.5 (s, CH_{3iPr}), 25.1 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 23.7 (s, CH_{3iPr}), -0.8 (s, Si-CH₃), -1.6 (s, Si-CH₃). C_{ipso} attached to boron atom could not be detected. ³¹P NMR (202 MHz, CD₂Cl₂): δ = 20.9 (s). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar}-F_{ortho}), -163.7 (t, J_{FF} = 20.4 Hz, C_{Ar}-F_{para}), -167.5 (t, J_{FF} = 18.1 Hz, m of C_{Ar}-F_{meta}). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 5.0 (s).

Synthesis of 7: In a J. Young NMR tube, to a solution of **5f** (50.0 mg, 0.042 mmol) in deuterated dichloromethane (0.3 mL) was added benzaldehyde (4.3 μL, 0.042 mmol). The reaction immediately proceeds to give adduct **7** in a mixture of 2 diastereomers in a 68:32 ratio. Suitable crystals for X-Ray diffraction were obtained by layering of pentane in dichloromethane. Product **7** was isolated as a white powder in 66 % yield (36 mg). Major isomer (68 %): ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.91-7.80 (m, 2H, CH_{Ph}), 7.78-7.68 (m, 2H, CH_{Ph}), 7.68-7.62 (m, 4H, CH_{Ph}), 7.50-7.40 (m, 3H, CH_{Ph}), 7.38-7.28 (m, 3H, CH_{Ph}), 7.23-7.15 (m, 2H, CH_{Ph}), 6.93-6.87 (m, 2H, CH_{Ph}), 6.39 (broad s, 1H, P-CH-O), 3.58 (sept., J_{HH} = 6.9 Hz, 1H, CH_{iPr}), 3.20 (sept., J_{HH} = 6.7 Hz, 1H, 2 CH_{iPr}), 2.92 (br, 2H, 2 CH_{bridgehead}), 2.01-1.92 (m, 1H, CH₂), 1.81-1.70 (m, 1H, CH₂), 1.58-1.48 (m, 2H, CH₂), 1.40 (d, J_{PH} = 6.9 Hz, 3H, CH_{3iPr}), 1.37-1.28 (m, 9H, 3 CH_{3iPr}), 1.27-1.23 (m, 1H, CH₂), 1.17-1.10 (m, 1H, CH₂), 0.67 (s, 3H, Si-CH₃), 0.02 (s, 3H, Si-CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 177.9 (d, J_{CP} = 5.2 Hz, N-C), 148.6 (br d, J_{CF} = 243.7 Hz, C_{Ar}-F), 147.6 (s, C_{dipp}), 146.8 (s, C_{dipp}), 138.6 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 136.6 (s, N-C_{dipp}), 136.5 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 135.8 (d, J_{CP} = 2.8 Hz, CH_{Ph}), 135.7 (d, J_{CP} = 2.8 Hz, CH_{Ph}),

134.7 (d, J_{CP} = 9.3 Hz, CH_{Ph}), 133.8 (d, J_{CP} = 9.1 Hz, CH_{Ph}), 131.2 (s, C_{ipso}(benzaldehyde)), 130.6 (d, J_{CP} = 12.2 Hz, CH_{Ph}), 130.3 (d, J_{CP} = 12.3 Hz, CH_{Ph}), 129.7 (d, J_{CP} = 11.9 Hz, CH_{Ph}), 129.6 (s, CH_{Ph}), 129.1 (d, J_{CP} = 2.6 Hz, CH_{Ph}), 127.9 (d, J_{CP} = 4.8 Hz, CH_{Ph}), 126.2 (s, 2 CH_{dipp}), 125.8 (s, 2 CH_{dipp}), 124.4 (br, B-C_{Ar}), 118.7 (d, J_{CP} = 86.1 Hz, P-C_{Ph}), 116.3 (d, J_{CP} = 83.0 Hz, P-C_{Ph}), 90.0 (d, J_{CP} = 91.5 Hz, C-P), 73.4 (d, J_{CP} = 62.0 Hz, CH-O), 49.1 (d, J_{CP} = 10.9 Hz, CH_{bridgehead}), 47.1 (d, J_{CP} = 5.7 Hz, CH₂), 46.6 (d, J_{CP} = 8.4 Hz, CH_{bridgehead}), 28.7 (s, CH_{iPr}), 28.6 (s, CH_{iPr}), 27.9 (s, CH₂), 26.6 (d, J_{CP} = 2.5 Hz, CH₂), 25.1 (s, CH_{3iPr}), 24.9 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 24.5 (s, CH_{3iPr}), 0.5 (s, Si-CH₃), -1.4 (s, Si-CH₃). ³¹P NMR (202 MHz, CD₂Cl₂): δ = 21.5 (s). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar}-F_{ortho}), -163.7 (t, J_{FF} = 20.4 Hz, C_{Ar}-F_{para}), -167.5 (t, J_{FF} = 18.1 Hz, C_{Ar}-F_{meta}). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 9.5 (s). Minor isomer (32 %): ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.91-7.80 (m, 1H, CH_{Ph}), 7.78-7.68 (m, 1H, CH_{Ph}), 7.68-7.62 (m, 4H, CH_{Ph}), 7.51-7.40 (m, 3H, CH_{Ph}), 7.38-7.28 (m, 3H, CH_{Ph}), 7.23-7.15 (m, 2H, CH_{Ph}), 7.10-7.03 (m, 2H, CH_{Ph}), 6.85-6.80 (m, 2H, CH_{Ph}), 6.39 (broad s, 1H, P-CH-O), 3.27 (sept., J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 3.20 (m, 1H, CH_{iPr}), 2.92 (br, 1H, CH_{bridgehead}), 2.81 (br, 1H, CH_{bridgehead}), 2.01-1.92 (m, 1H, CH₂), 1.92-1.82 (m, 1H, CH₂), 1.79-1.70 (m, 1H, CH₂), 1.58-1.48 (m, 1H, CH₂), 1.37-1.28 (m, 9H, 3 CH_{3iPr}), 1.21 (d, J_{PH} = 6.8 Hz, 3H, CH_{3iPr}), 1.17-1.10 (m, 1H, CH₂), 1.03-0.96 (m, 1H, CH₂), 0.85 (s, 3H, Si-CH₃), 0.09 (s, 3H, Si-CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 177.7 (d, J_{CP} = 5.2 Hz, N-C), 148.6 (br d, J_{CF} = 243.7 Hz, C_{Ar}-F), 147.5 (s, C_{dipp}), 146.5 (s, C_{dipp}), 138.6 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 137.1 (s, C_{dipp}), 136.5 (br d, J_{CF} = 244.4 Hz, C_{Ar}-F), 135.7 (d, J_{CP} = 2.8 Hz, CH_{Ph}), 135.4 (d, J_{CP} = 3.0 Hz, CH_{Ph}), 134.8 (d, J_{CP} = 9.8 Hz, CH_{Ph}), 133.6 (d, J_{CP} = 9.3 Hz, CH_{Ph}), 132.7 (s, *ipso* of (C₆H₅)₂benzaldehyde), 131.0 (d, J_{CP} = 11.9 Hz, CH_{Ph}), 130.8 (d, J_{CP} = 3.3 Hz, CH_{Ph}), 130.5 (d, J_{CP} = 3.8 Hz, CH_{Ph}), 129.5 (s, CH_{Ph}), 129.3 (d, J_{CP} = 3.1 Hz, CH_{Ph}), 126.9 (s, J_{CP} = 4.2 Hz, CH_{Ph}), 125.8 (s, CH_{dipp}), 125.7 (s, CH_{dipp}), 124.4 (br, *ipso* of BAr), 119.7 (d, J_{CP} = 82.2 Hz, P-C_{Ph}), 115.2 (d, J_{CP} = 87.4 Hz, P-C_{Ph}), 83.8 (d, J_{CP} = 93.5 Hz, C-P), 73.5 (d, J_{CP} = 59.6 Hz, P-CH-O), 49.8 (d, J_{CP} = 10.5 Hz, CH_{bridgehead}), 48.0 (d, J_{CP} = 10.4 Hz, CH_{bridgehead}), 46.0 (d, J_{CP} = 4.0 Hz, CH₂), 28.7 (s, CH_{iPr}), 28.5 (s, CH_{iPr}), 28.3 (s, CH₂), 26.4 (d, J_{CP} = 2.5 Hz, CH₂), 25.4 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 24.0 (s, CH_{3iPr}), -1.7 (s, Si-CH₃), -3.5 (s, Si-CH₃). ³¹P NMR (202 MHz, CD₂Cl₂): δ = 22.2 (s). ¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -133.0 (br, C_{Ar}-F_{ortho}), -163.7 (t, J_{FF} = 20.4 Hz, C_{Ar}-F_{para}), -167.5 (t, J_{FF} = 18.1 Hz, C_{Ar}-F_{meta}). ¹¹B NMR (160 MHz, CD₂Cl₂): δ = -16.6 (s, BAr). ²⁹Si NMR (99 MHz, CD₂Cl₂): δ = 8.9 (s).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Spectroscopic and X-ray data (PDF), X-ray of: **3** (CIF); **4b** (CIF); **4c** (CIF); **4d** (CIF), **4e** (CIF) and **7** (CIF).

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Notes

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