# **ORGANOMETALLICS**

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

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an efficient donation of the phosphine group toward the electrondeficient 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 Flexible ligand framework  $Ph_2P: + Si < Ph_2P: + Si < P$ 

easily improved using less donating phosphine ligands. Of particular interest, thanks to the flexible ligand framework, the phosphinestabilized 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 Reed and Lambert groups have achieved a major synthetic challenge.<sup>1</sup> Indeed, because of their exceptionally high Lewis acidity, silylium ions have remained elusive species for a long time.<sup>2</sup> To take advantage of these unique species in synthesis or catalysis, their reactivity needs to be tamed.<sup>3</sup> 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).<sup>4</sup> 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 alkyl fluorides were found to be efficiently catalyzed by intramolecularly stabilized silyl cations III–V.<sup>5</sup> These species are also capable of catalyzing Diels–Alder reactions, and the ferrocene-stabilized system VI developed by the Oestreich group is particularly efficient for low-temperature cycloaddition reactions with  $\alpha$ , $\beta$ -unsaturated ketones.<sup>6</sup> 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.<sup>7</sup>

One of our main objectives is the stabilization of electrondeficient species,<sup>8</sup> and recently, a framework based on norbornene was designed to stabilize silylenes using phosphines as Lewis bases.<sup>9</sup> Of special interest, we have shown that, due to the weak coordination of the 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) center<sup>10</sup> and the reversible oxidation addition/reductive elimination of R<sub>3</sub>SiH at the Si(II) center.<sup>11</sup> The key features of this system are the moderate structural flexibility and the rigid planar structure of the enamino phosphine fragment, which results in a particular  $P \rightarrow Si$ interaction. We have thus considered the synthesis of the



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novel phosphine-stabilized silylium ions 4, which despite a strong P–Si interaction behave as frustrated Lewis pairs and allows the synthesis of seven- to nine-membered heterocycles.

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

Scheme 1. Synthesis of Silylium Precursors 2



Attempts to generate silvlium ions via the classical Bartlett– Schneider–Condon method<sup>2</sup> 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 4position of a phenyl group (Scheme 2). The same type of reaction between bulky phosphines (PtBu<sub>3</sub> and PCy<sub>3</sub>) and trityl salts was already observed by Stephan et al.<sup>12</sup>

#### 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 characteristic of a single bond, and the cyclohexadiene ring shows alternate single- and double-bond lengths, planar environments around C35 and C38 ( $\Sigma$  = 359.9 and 360.0°, respectively), and a tetrahedral environment at C32.

The expected silvlium ions **4** can be easily obtained following the methodology of Kira and Sakurai,<sup>13</sup> starting from the corresponding chlorosilanes  $2\mathbf{b}-\mathbf{e}$ , just by halide abstraction using potassium borate salt (Scheme 3).

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.

Silylium ions 4c,d with two different substituents on the Si atom (4c,  $R^2 = Cl$ ,  $R^3 = Me$ ; 4d,  $R^2 = Cl$ ,  $R^3 = H$ ) were expected to be formed as diastereomer couples since the



**Figure 2.** Molecular structure of **3.** Thermal ellipsoids represent 30% probability. H atoms (except on Si1 and C32), solvent molecules, and the counterion  $[B(C_6F_5)_4]^-$  are 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).

#### Scheme 3. Preparation of Silylium ions 4b-e and 5f,g



Table 1. NMR Data of Silylium Ions 4b-e (in CD<sub>2</sub>Cl<sub>2</sub> at 298 K)

compd	$\mathbb{R}^2$	R <sup>3</sup>	<sup>31</sup> P (ppm)	<sup>29</sup> Si (ppm)	$J_{\rm PSi}~({\rm Hz})$		
4b	Me	Me	39.6	6.1	132.0		
$4c^{a}$	Cl	Me	30.2, 30.0	-0.3, -2.1	172.6, 171.2		
4d <sup>b</sup>	Cl	Н	28.4	-22.9	169.5		
4e	Cl	Cl	21.8	-21.6	237.4		
<sup><i>a</i></sup> dr = 50:50. <sup><i>b</i></sup> Only one diastereomer is formed.							

silylium center is stereogenic. A 50:50 diastereomeric ratio was obtained for 4c, but in the case of 4d, a single diastereomer was formed. With regard to the strong phosphine—silylium ion interaction (*vide infra*), the epimerization of 4 at the chiral silicon center through P—Si bond dissociation is difficult to consider. 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 $\rightarrow$ Si interaction was clearly indicated by the significantly high field shifted signals in <sup>29</sup>Si and <sup>31</sup>P NMR (<sup>29</sup>Si, -87.2 ppm; <sup>31</sup>P, 43.1 ppm) with a large  $J_{Si-P}$  coupling constant (223.8 Hz) in comparison to those observed for 2c showing typical silane and phosphine signals (<sup>29</sup>Si, -5.5 ppm; <sup>31</sup>P, 111.3 ppm) in agreement with a tetracoordinate Si atom without a P $\rightarrow$ 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 lesshindered equatorial position. The formation of **4d** should take place exclusively, keeping the configuration at the Si center, via the cleavage of the 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 a P→Si interaction, the abstraction of the Cl anion is not selective and thus affords **4c** as a mixture of two diastereomers.

An analysis of these spectroscopic data indicates that silylium **4e**, which bears two strongly electron withdrawing chloride atoms, shows the strongest P–Si interaction, as indicated by a relatively shielded <sup>31</sup>P NMR chemical shift ( $\delta$ 21.8 ppm) and a large silicon–phosphorus coupling constant ( $J_{PSi} = 237.4$  Hz). The <sup>29</sup>Si NMR chemical shift is also a good probe to evaluate the Lewis acidity of silylium ions.<sup>14</sup> In this series, **4b** exhibits an enhanced Lewis acidity, as indicated by the <sup>29</sup>Si NMR chemical shift, which appears at  $\delta$  6.1 ppm, among the more deshielded signals and the smallest silicon– phosphorus coupling constant ( $J_{PSi} = 132.0$  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).

The X-ray diffraction data are in good agreement with the spectroscopic data. Indeed, the longest Si1–P1 bond length (2.322(1) Å) of the series was found in **4b**, suggesting a weak Si–P interaction: in other words, the strongest Lewis acid of the series. It is worth noting that the modification of the silylium center substituent ( $\mathbb{R}^2$  and  $\mathbb{R}^3$ ) has a rather weak effect 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** (PR<sub>2</sub> = PPh<sub>2</sub>) have been prepared using the same synthetic methodology as for **4** (Scheme 3).

The new silylium ions **5** were obtained in nearly quantitative yields, in the case of **5g** ( $R^2 = Cl$ ,  $R^3 = Me$ ) 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 <sup>29</sup>Si



Figure 3. Molecular structures of 4b-e. Thermal ellipsoids represent 30% probability. Counterions, solvent molecules, disordered atoms, and hydrogen atoms are omitted for clarity (except the hydrogen atom on the silicon atom of 4d).

NMR signals at  $\delta$  27.2 ppm for **5f** and  $\delta$  15.4 and 15.3 ppm for **5g** in comparison 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** ( $R^2 = R^3 = Me$ ).

Although, the ability of these two families of silylium ions as catalysts of Diels–Alder reactions between cyclohexadiene or 2,3-dimethylbutadiene and methyl acrylate (10 mol % of silylium 4 or 5 in  $\text{CDCl}_3$ )<sup>4a,6,15</sup> 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 <sup>31</sup>P NMR analysis shows the complete disappearance of the silylium signal (–20.8 ppm) and a new single signal appearing at  $\delta$  20.9 ppm. In fact, silylium ion **5f** reacts with 1 equiv of methyl acrylate at 50 °C, leading to an insertion reaction of the conjugated carbonyl into the P $\rightarrow$ Si dative bond. Silylium cation **5f**, acting as a frustrated Lewis pair (FLP),<sup>7b,16</sup> quantitatively affords the original nine-membered heterocycle **6**, which loses the Lewis acid character (silane structure), probably explaining the absence of any catalytic activity (Scheme 5).

The <sup>13</sup>C NMR spectrum is particularly informative with the peculiar chemical shift of the ketene acetal type part CH==C of **6**, with chemical shift at  $\delta$  67.8 ppm ( $J_{CP}$  = 10.6 Hz) for the primary and at  $\delta$  156.9 ppm ( $J_{CP}$  = 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 Sf.<sup>17</sup> The corresponding seven-membered-ring species 7 was isolated as a mixture of two diastereomers in a 68:32 ratio and fully

compd	P1-C1	C1-C2	C2-N1	N1-Si1	Si1-P1	$Si1-R^{2a}$	$Si1-R^{3b}$
4b	1.730(3)	1.369(4)	1.371(4)	1.781(3)	2.322(1)	1.844(4)	1.844(4)
4c	1.708(12)	1.383(16)	1.423(16)	1.731(11)	2.302(7)	1.952(13)	1.73(3)
4d	1.737(9)	1.370(10)	1.355(6)	1.734(4)	2.287(2)	2.067(2)	1.44(8)
4e	1.711(4)	1.368(5)	1.368(4)	1.730(3)	2.293(1)	2.014(1)	2.011(1)
<sup><i>a</i></sup> Si1-R <sup>2</sup> : Si-CH <sub>3</sub> (4b); Si-Cl (4c-e). <sup><i>b</i></sup> Si1-R <sup>3</sup> : Si-CH <sub>3</sub> (4b,c); Si-H (4d); Si-Cl (4e).							

Table 2. Main Bond Lengths (in Å) Obtained from X-ray Diffraction Analysis of 4b-e

Table 3. Experimental NMR Parameters of Silylium Ions Sf,g (in CD<sub>2</sub>Cl<sub>2</sub> at 298 K)

compd	$\mathbb{R}^2$	R <sup>3</sup>	<sup>31</sup> P (ppm)	<sup>29</sup> Si (ppm)	$J_{\rm PSi}$ (Hz)
5f	Me	Me	-20.8	27.2	82.1
5g <sup>a</sup>	Cl	Me	-24.3, -24.1	15.4, 15.3	124.6, 117.4
$^{a}$ dr = 76	:24.				

Scheme 5. Reaction of Silylium Ion 5f with Carbonyl Derivatives





**Figure 4.** Molecular structure of 7. Thermal ellipsoids represent 30% probability. The counterion, disordered atoms, and hydrogen atoms are omitted for clarity (except H34). Selected bond lengths (Å) and angles (deg): 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).

characterized by NMR spectroscopy; 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  $P \rightarrow Si$  interaction as well as the moderate flexibility of the ligand framework. Indeed, such a flexibility of the 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 wider interior angles of the P1–C1–C2–N1–Si1 fragment (P1–C1–C2 132.36°, C1–C2–N1 130.78°, and C2–N1–Si1 122.63°) in 7, in comparison with those of the phosphinesilylium ion complex 4b (P1–C1–C2 116.82°, C1–C2–N1 125.50°, and C2–N1–Si1 113.84°). However, 5f is not reactive enough to activate H<sub>2</sub>, 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.<sup>18</sup> Similar FLP-type reactions were also observed for phosphine-stabilized germylene and stannylenes with a strained three-membered cyclic structure.<sup>19</sup>

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 **Sf** 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, has been described. As expected, the moderate structural flexibility favors the enamino phosphine donation to the 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 more weakly donating phosphine ligand. Of particular interest, thanks to the flexible ligand framework, and despite an efficient intramolecular stabilization, the base-stabilized silylium ion **Sf** behaves as a frustrated Lewis pair 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. <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, <sup>28</sup>Si, and <sup>31</sup>P NMR spectra were recorded on Bruker Avance II 300 MHz, Avance III HD 400 MHz, and Avance I and II 500 MHz spectrometers. <sup>1</sup>H, <sup>29</sup>Si, and <sup>13</sup>C NMR chemical shifts are reported in parts per million (ppm) relative to Me<sub>4</sub>Si as an internal standard. <sup>11</sup>B NMR downfield chemical shifts are expressed in ppm relative to BF<sub>3</sub>·Et<sub>2</sub>O. <sup>19</sup>F chemical shifts are reported in ppm relative to CFCl<sub>3</sub> as an external standard. <sup>31</sup>P NMR chemical shifts are expressed in ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. <sup>1</sup>H and <sup>13</sup>C resonance signals were attributed by means of 2D COSY, HSQC, and HMBC experiments. Mass spectra were recorded on a Hewlett-Packard 5989A spectrometer. All commercially available reagents were used without further purification unless noted otherwise.

**Synthesis of 1.**  $PR_2 = P(NtBu)_2SiMe_2$ . To a stirred solution of imine<sup>20</sup> (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

warmed to room temperature over 1 h with stirring. The solution was cooled to -78 °C, and chlorophosphine (9.9 g, 37.1 mmol) was added. The mixture was warmed to room temperature, and the solvent was removed under vacuum. The solid was washed with acetonitrile (3 × 20 mL), dried, and dissolved in pentane, and this solution was 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.<sup>20</sup>

 $PR_2 = PPh_2$ . 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 the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 1 h and then cooled again to -80 °C, and chlorodiphenylphosphine (6.84 mL, 37.1 mmol) was added dropwise. The resulting solution was warmed to room temperature and stirred for 1 h, and 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.<sup>21</sup>

Synthesis of 2a ( $R^1 = H$ ;  $\dot{R}^2 = R^3 = Me$ ). To a solution of iminophosphine 1 (2.00 g, 4.0 mmol) in THF (25 mL) was added dropwise at -80 °C a 1.6 M solution of *n*-butyllithium in hexane (2.5 mL, 4.0 mmol), and the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 1 h and then cooled again to -80 °C, and chlorodimethylsilane (0.44 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed to room temperature and stirred for 1 h, and then the solvent was removed under vacuum. Product 2a was extracted with heptane from the crude mixture, and pale yellow crystals were obtained from a saturated heptane solution at -30 °C (1.20 g, 54% yield). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  7.15–7.01 (m, 3H,  $CH_{dipp}$ ), 5.55 (dsept, <sup>2</sup> $J_{PH}$  = 15.3 Hz,  ${}^{3}J_{H-H} = 2.7$  Hz, 1H, SiH), 3.86 (s, 1H, CH<sub>bridgehead</sub>), 3.43 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H,  $CH_{iPr}$ ), 3.32 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H, CH<sub>iPr</sub>), 2.56 (s, 1H, CH<sub>bridgehead</sub>), 1.98-1.71 (m, 2H, CH<sub>2</sub>), 1.58-1.47 (m, 1H, CH<sub>2</sub>), 1.47-1.38 (m, 2H, CH<sub>2</sub>), 1.34 (s, 9H, CH<sub>3tBu</sub>), 1.32 (s, 9H, CH<sub>3tBu</sub>), 1.28–1.16 (m, 12H, CH<sub>3iPr</sub>), 1.10–1.03 (m, 2H,  $CH_2$ ), 0.56 (dd,  ${}^{3}J_{HH} = 2.8$  Hz,  ${}^{3}J_{PH} = 4.4$  Hz, 3H, SiH $-CH_3$ ), 0.50 (s, 6H, Si-CH<sub>3</sub>), 0.14 (dd,  ${}^{3}J_{HH} = 3.2$  Hz,  ${}^{3}J_{PH} = 1.9$  Hz, 3H, SiH-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz,  $C_6D_6$ ):  $\delta$  163.9 (d, <sup>2</sup> $J_{CP}$  = 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, <sup>1</sup> $J_{CP}$  = 56.5 Hz, C-P), 50.9 (d,  ${}^{2}J_{CP} = 13.7 \text{ Hz}, C_{tBu}$ , 50.7 (d,  ${}^{2}J_{CP} = 11.3 \text{ Hz}, C_{tBu}$ ), 48.1 (d,  ${}^{2}J_{CP} = 3.5$ Hz,  $CH_{bridgehead}$ ), 47.0 (s,  $CH_2$ ), 42.9 (s,  $CH_{bridgehead}$ ), 32.7 (d,  ${}^{3}J_{CP}$  = 4.9 Hz,  $C\dot{H}_{3tBu}$ ), 32.5 (d,  ${}^{3}J_{CP}$  = 5.2 Hz,  $CH_{3tBu}$ ), 28.8 (s,  $CH_{2}$ ), 27.9 (s, 2 CH<sub>iPr</sub>), 26.8 (s, CH<sub>2</sub>), 25.3 (s, CH<sub>3IPr</sub>), 25.1 (s, CH<sub>3IPr</sub>), 24.8 (s, CH<sub>3IPr</sub>), 24.6 (s, CH<sub>3IPr</sub>), 8.0 (d,  ${}^{3}J_{CP} = 5.3$  Hz, Si-CH<sub>3</sub>), 6.3 (s, Si-CH<sub>3</sub>), 0.3 (d,  ${}^{2}J_{CP} = 24.5$  Hz, SiH-CH<sub>3</sub>), 0.0 (d,  ${}^{2}J_{CP} = 12.5$  Hz, SiH-CH<sub>3</sub>), 0.1 (d,  ${}^{2}J_{PH} = 15.3$  Hz). <sup>29</sup>Si NMR (60 MHz,  $C_6D_6$ ):  $\delta$  8.1 (s, SiMe<sub>2</sub>), -9.2 (d, <sup>1</sup>J<sub>SiP</sub> = 15.8 Hz, SiMe<sub>2</sub>H). Mp: 209 °C.

Synthesis of 2b ( $R^1 = CI$ ;  $R^2 = R^3 = Me$ ). To a solution of iminophosphine 1 ( $PR_2$  = cyclic diaminophosphine) (2.00 g, 4.0 mmol) in THF (20 mL) was added dropwise at -80 °C a 1.6 M solution of n-butyllithium in hexane (2.5 mL, 4.0 mmol), and the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 1 h, and then cooled again to -80 °C, and dichlorodimethylsilane (0.48 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed to room temperature and stirred for 1 h, and 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). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 328 K): δ 7.31-7.25 (m, 1H, CH<sub>dipp</sub>), 7.20-7.14 (m, 2H,  $CH_{dipp}$ ), 3.77 (s, 1H,  $CH_{bridgehead}$ ), 3.40 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H,  $CH_{iPr}$ ), 3.25 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H,  $CH_{iPr}$ ), 2.51 (s, 1H,  $CH_{bridgehead}$ ), 1.84–1.65 (m, 2H,  $CH_{2}$ ), 1.52–1.36 (m, 3H,  $CH_{2}$ ), 1.35–1.26 (m, 6H, CH<sub>3iPr</sub>), 1.31 (s, 9H, CH<sub>3tBu</sub>), 1.28 (s, 9H,  $CH_{3tBu}$ ), 1.25 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 12H,  $CH_{3iPr}$ ), 1.24 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 12H, CH<sub>3iPr</sub>), 1.06–1.01 (m, 1H, CH<sub>2</sub>), 0.72 (br, 6H, SiCl-CH<sub>3</sub>),

0.51 (s, 3H, Si–CH<sub>3</sub>), 0.47 (s, 3H, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 328 K): δ 161.4 (d, <sup>2</sup>J<sub>CP</sub> = 26.0 Hz, N–C), 148.4 (s, C<sub>dipp</sub>), 147.4 (s, C<sub>dipp</sub>), 142.1 (s, N–C<sub>dipp</sub>), 127.5 (s, CH<sub>dipp</sub>), 124.4 (s, CH<sub>dipp</sub>), 124.2 (s, CH<sub>dipp</sub>), 121.2 (d, <sup>1</sup>J<sub>CP</sub> = 58.5 Hz, C-P), 50.9 (d, <sup>2</sup>J<sub>CP</sub> = 13.6 Hz, C<sub>tBu</sub>), 50.7 (d, <sup>2</sup>J<sub>CP</sub> = 11.5 Hz, C<sub>tBu</sub>), 48.6 (d, <sup>2</sup>J<sub>CP</sub> = 3.2 Hz, CH<sub>bridgehead</sub>), 46.7 (s, CH<sub>2</sub>), 42.8 (s, CH<sub>bridgehead</sub>), 32.6 (d, <sup>3</sup>J<sub>CP</sub> = 4.6 Hz, CH<sub>3tBu</sub>), 23.2 (d, <sup>3</sup>J<sub>CP</sub> = 5.3 Hz, CH<sub>3tBu</sub>), 28.2 (s, CH<sub>2</sub>), 27.9 (s, CH<sub>3tPr</sub>), 27.7 (s, CH<sub>iPr</sub>), 26.8 (s, CH<sub>2</sub>), 25.5 (s, CH<sub>3tPr</sub>), 25.2 (s, CH<sub>3tPr</sub>), 24.9 (s, CH<sub>3tPr</sub>), 8.0 (d, <sup>3</sup>J<sub>CP</sub> = 5.3 Hz, Si–CH<sub>3</sub>), 6.3 (s, Si–CH<sub>3</sub>), 6.1 (br d, <sup>2</sup>J<sub>CP</sub> = 22.0 Hz, 2 SiCl–CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, 328 K): δ 114.0 (br). <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>, 328 K): δ 10.3 (br, SiMe<sub>2</sub>Cl), 9.1 (s, SiMe<sub>2</sub>).

Synthesis of 2c ( $R^1 = R^2 = Cl$ ;  $R^3 = Me$ ). To a solution of iminophosphine 1 ( $PR_2$  = cyclic diaminophosphine) (2.00 g, 4.0 mmol) in THF (20 mL) was added dropwise at -80 °C a 1.6 M solution of n-butyllithium in hexane (2.5 mL, 4.0 mmol), and the mixture was stirred for 1 h. The crude mixture was warmed to room temperature and stirred for 1 h and then cooled to -80 °C, and trichloromethylsilane (0.47 mL, 4.0 mmol) was added dropwise. The resulting solution was warmed to room temperature and stirred for 1 h, and 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). <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ):  $\delta$  7.33–7.27 (m, 1H,  $CH_{dipp}$ ), 7.20–7.14 (m, 2H,  $CH_{dipp}$ ), 3.73 (s, 1H,  $CH_{bridgehead}$ ), 3.31 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 3.18 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H,  $CH_{iPr}$ ), 2.43 (s, 1H, CH<sub>bridgehead</sub>), 1.80–1.63 (m, 2H, CH<sub>2</sub>), 1.47–1.31 (m, 3H, CH<sub>2</sub>), 1.28 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 3H, CH<sub>3iPr</sub>), 1.26 (s, 9H, CH<sub>3tBu</sub>), 1.25–1.18 (m, 3 × 3H,  $CH_{3iPr}$  overlapped by  $CH_{3tBu}$ ), 1.23 (s, 9H,  $CH_{3tBu}$ ), 1.07 (br s, 3H, SiCl<sub>2</sub>-CH<sub>3</sub>), 1.03-1.00 (m, 1H, CH<sub>2</sub>), 0.48 (s, 3H, Si- $CH_3$ ), 0.44 (s, 3H, Si– $CH_3$ ). <sup>13</sup>C NMR (126 MHz,  $CD_2Cl_2$ ):  $\delta$  159.6  $(d, {}^{2}J_{CP} = 25.8 \text{ Hz}, \text{ N-}C)$ , 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,  ${}^{1}J_{CP} = 56.5$  Hz, C-P), 51.1 (d,  ${}^{2}J_{CP} = 13.4$  Hz,  $C_{tBu}$ ), 50.9 (d,  ${}^{2}J_{CP}$  = 11.6 Hz,  $C_{tBu}$ ), 48.6 (d,  ${}^{2}J_{CP}$  = 2.9 Hz,  $CH_{bridgehead}$ ), 47.1 (s, CH<sub>2</sub>), 43.1 (s, CH<sub>bridgehead</sub>), 32.6 (d,  ${}^{3}J_{CP} = 4.5$  Hz, CH<sub>3tBu</sub>), 32.2 (d,  ${}^{3}J_{CP}$  = 5.1 Hz, CH<sub>3tBu</sub>), 28.4 (s, 2 CH<sub>iPr</sub>), 28.2 (s, CH<sub>2</sub>), 28.1 (s, 2  $(CH_{iPr})$ , 26.9 (s,  $CH_2$ ), 25.7 (s,  $CH_{3iPr})$ , 25.3 (s,  $CH_{3iPr})$ , 24.7 (s,  $CH_{3iPr})$ , 24.6 (s,  $CH_{3iPr})$ , 9.7 (d,  ${}^2J_{CP}$  = 24.9 Hz, SiCl- $CH_3$ ), 7.9 (d,  ${}^{3}J_{CP}$  = 5.2 Hz, Si-CH<sub>3</sub>), 6.2 (s, Si-CH<sub>3</sub>).  ${}^{31}P$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 111.3 (s). <sup>29</sup>Si NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 10.1 (s,  $SiMe_2$ ), -5.5 (s,  $SiMeCl_2$ ).

Synthesis of 2d ( $R^1 = R^2 = Cl; R^3 = H; PR_2 = Cyclic Diaminophosphine$ ). Intense yellow solid (1.728 g, 72%). Spectroscopic data are in perfect agreement with the values already reported.<sup>10a</sup>

Synthesis of 2e ( $R^1 = R^2 = R^3 = CI$ ). Orange crystals (8.6 g, 66%). Spectroscopic data are in perfect agreement with the values already reported.<sup>22</sup>

Synthesis of 2f ( $R^1 = Cl$ ;  $R^2 = R^3 = Me$ ). To a solution of iminophosphine 1 ( $PR_2 = PPh_2$ ) (1.01 g, 2.2 mmol) in THF (25 mL) was added dropwise at -80 °C a 1.6 M solution of n-butyllithium in hexane (1.4 mL, 2.2 mmol), and the mixture was stirred for 1 h. The reaction mixture was then warmed to room temperature and stirred for 1 h and then cooled again to -80 °C and dichlorodimethylsilane (0.27 mL, 2.2 mmol) was added dropwise. The resulting solution was warmed to room temperature and stirred for 1 h before removal of the solvent under vacuum. Product 2f was extracted with heptane and colorless crystals were obtained from a saturated heptane solution at -30 °C (1.11 g, 88% yield). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.45-6.97 (m, 13H, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> + 3 CH<sub>dipp</sub>), 3.70 (s, 1H, CH<sub>bridgehead</sub>), 3.36-3.12 (br, 2H,  $CH_{iPr}$ ), 3.06 (s, 1H,  $CH_{bridgehead}$ ), 1.89–1.71 (m, 1H + 1H, CH<sub>2</sub>), 1.60–1.42 (m, 2H, CH<sub>2</sub>), 1.35–1.28 (m, 1H, CH<sub>2</sub>), 1.25 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 3H,  $CH_{3iPr}$ ), 1.15 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 3H,  $CH_{3iPr}$ ), 1.04 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 3H,  $CH_{3iPr}$ ), 0.82–0.20 (br, 6H + 1H, 2 Si–  $CH_3 + CH_2$ ), 0.74 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 3H,  $CH_{3iPr}$ ).  ${}^{13}C$  NMR (75 MHz,  $CD_2Cl_2$ ):  $\delta$  165.0 (d,  ${}^{2}J_{CP} = 21.2$  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,  ${}^{1}J_{CP}$  = 12.5 Hz, P–CPh), 140.4 (d,  ${}^{4}J_{CP}$  = 3.6 Hz, N– $C_{dipp}$ ), 138.6 (d,  ${}^{1}J_{CP}$  = 17.4 Hz, P– $C_{Ph}$ ), 136.8 (d,  $J_{CP}$  = 25.2 Hz,  $CH_{Ph}$ ), 131.6 (d,  $J_{CP}$  = 15.1 Hz,

CH<sub>Ph</sub>), 129.1 (s, CH<sub>Ph</sub>), 128.2 (s, CH<sub>Ph</sub>), 127.9 (d,  $J_{CP} = 2.5$  Hz, CH<sub>Ph</sub>), 127.8 (d, JCP = 3.0 Hz, CH<sub>Ph</sub>), 126.3 (s, CH<sub>dipp</sub>), 125.4 (s, CH<sub>dipp</sub>), 124.6 (s, CH<sub>dipp</sub>), 107.2 (d,  ${}^{1}J_{CP} = 21.5$  Hz, C–P), 49.1 (d,  ${}^{3}J_{CP} = 5.5$  Hz, CH<sub>bridgehead</sub>), 47.2 (s, CH<sub>2</sub>), 47.0 (d,  ${}^{3}J_{CP} = 5.2$  Hz, CH<sub>bridgehead</sub>), 28.5 (s, CH<sub>iPr</sub>), 28.2 (s, CH<sub>iPr</sub>), 27.7 (s, CH<sub>2</sub>), 27.6 (s, CH<sub>2</sub>), 25.9 (s, CH<sub>3iPr</sub>), 25.0 (s, CH<sub>3iPr</sub>), 24.9 (s, CH<sub>3iPr</sub>), 24.6 (d,  $J_{CP} = 5.8$  Hz, CH<sub>3iPr</sub>), 5.1 (br, Si–CH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –25.4. <sup>29</sup>Si NMR (60 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  11.5. Mp: 101.1 °C.

Synthesis of 2g ( $R^1 = R^2 = CI$ ;  $R^3 = Me$ ). To a solution of iminophosphine 1 ( $PR_2 = PPh_2$ ) (2.94 g, 6.5 mmol) in THF (25 mL) was added dropwise at -80 °C a 1.6 M solution of *n*-butyllithium in hexane (4.14 mL, 6.5 mmol), and the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 1 h and then cooled again to -80 °C, and trichloromethylsilane (0.78 mL, 6.5 mmol) was added dropwise. The resulting solution was warmed 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). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.43– 6.90 (m, 13H,  $P(C_6H_5)_2$ ) + 3  $CH_{dipp}$ ), 3.91 (s, 1H,  $CH_{bridgehead}$ ), 3.42 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 3.28 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H, CH<sub>iPr</sub>), 3.08 (s, 1H, CH<sub>bridgehead</sub>), 1.91-1.76 (m, 1H, CH<sub>2</sub>), 1.75-1.50 (m, 2H, CH<sub>2</sub>), 1.45–1.30 (m, 1H, CH<sub>2</sub>), 1.24 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 3H,  $CH_{3iPr}$ ), 1.17 (d,  ${}^{3}J_{HH}$  = 6.7 Hz, 3H,  $CH_{3iPr}$ ), 1.09 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 3H,  $CH_{3iPr}$ ), 0.95–0.80 (m, 1H,  $CH_2$ ), 0.78 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 3H,  $CH_{3iPr}$ ), 0.44 (s, 3H, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 162.7 (d,  ${}^{2}J_{CP} = 20.7$  Hz, N–C), 149.2 (d,  ${}^{5}J_{CP} = 6.2$  Hz,  $C_{dipp}$ ), 146.2  $(d, {}^{5}J_{CP} = 2.2 \text{ Hz}, C_{dipp}), 143.4 (d, {}^{1}J_{CP} = 12.4 \text{ Hz}, P-C_{Ph}), 138.9 (d, {}^{1}J_{CP} = 12.4 \text{ Hz}), 138.9 (d, {}^{$  ${}^{4}J_{CP}$  = 3.8 Hz C–N), 138.1 (d,  ${}^{1}J_{CP}$  = 17.6 Hz, P–C<sub>Ph</sub>), 136.9 (d,  $J_{CP}$ = 25.4 Hz,  $CH_{Ph}$ ), 131.7 (d,  $J_{CP}$  = 15.1 Hz,  $CH_{Ph}$ ), 129.3 (s,  $CH_{Ph}$ ), 129.1 (s,  $CH_{Ph}$ ), 128.0 (d,  $J_{CP}$  = 6.1 Hz,  $CH_{Ph}$ ) overlapped by deuterated solvent), 127.9 (d,  $J_{CP}$  = 11.9 Hz, CH<sub>Ph</sub> overlapped by deuterated solvent), 126.5 (s,  $CH_{dipp}$ ), 125.4 (s,  $CH_{dipp}$ ), 125.1 (s,  $CH_{dipp}$ ), 111.1 (d,  ${}^{1}J_{CP} = 24.0 \text{ Hz}$ , C-P), 49.2(d,  ${}^{3}J_{CP} = 4.9 \text{ Hz}$ ,  $CH_{bridgehead}$ ), 47.4 (s,  $CH_2$ ), 47.1(d,  ${}^2J_{CP}$  = 5.1 Hz,  $CH_{bridgehead}$ ), 28.7  $(s, CH_{iPr})$ , 28.2  $(s, CH_{iPr})$ , 27.5  $(s, CH_2)$ , 27.4  $(s, CH_2)$ , 26.0  $(d, J_{CP} =$ 6.2 Hz, CH<sub>3iPr</sub>), 25.1 (s, CH<sub>3iPr</sub>), 24.8 (s, CH<sub>3iPr</sub>), 24.6 (s, CH<sub>3iPr</sub>), 6.9 (s, Si–CH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –26.1. <sup>29</sup>Si NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ –5.0. Mp: 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 turned 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 characterize it. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K): δ 7.44-7.09 (m, 13H, C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and CH<sub>dipp</sub>), 6.95 (br, 2H, P-CH-CH=CH), 6.13 (br, 2H, P-CH-CH=CH), 5.20 (d,  ${}^{2}J_{PH}$  = 36.2 Hz, 1H, P–CH), 5.04 (br s, 1H, SiH), 3.79 (br, 1H, CH<sub>bridgehead</sub>), 3.22 (br, 1H, CH<sub>iPr</sub>), 3.06 (br, 1H, CH<sub>iPr</sub>), 2.96 (br, 1H, CH<sub>bridgehead</sub>), 2.07-1.61 (br(m), 3H, 2 CH<sub>2</sub>), 1.57-0.97 (m, 15H, 4 CH<sub>3iPr</sub> and 2 CH<sub>2</sub>), 1.41 (s, 9H, CH<sub>3tBu</sub>), 1.34 (s, 9H, CH<sub>3tBu</sub>), 0.77 (s, 3H, Si-CH<sub>3</sub>), 0.76 (s, 3H, Si-CH<sub>3</sub>), 0.46 (s, 3H, SiH-CH<sub>3</sub>), -0.10 (s, 3H, SiH $-CH_3$ ). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$ 174.0 (d,  ${}^{2}J_{CP}$  = 7.1 Hz, N-C), 147.8 (br d,  $J_{CF}$  = 240.0 Hz,  $C_{Ar}$ -F), 147.0 (s,  $C_{dipp}$ ), 145.8 (s,  $C_{dipp}$ ), 143.4 (d,  $J_{CP}$  = 12.7 Hz,  $C(Ph)_2$ ), 140.7 (d,  $J_{CP} = 4.4$  Hz,  $C_{Ph}$ ), 140.6 (d,  $J_{CP} = 4.3$  Hz,  $C_{Ph}$ ), 138.7 (s,  $\begin{array}{l} \text{N-}C_{\text{dipp}}, \text{ 138.2 (br d, } J_{\text{CF}} = 245.7 \text{ Hz}, C_{Ar}\text{-F}), \text{ 136.1 (br d, } J_{\text{CF}} = 245.1 \text{ Hz}, C_{Ar}\text{-F}), \text{ 136.1 (br d, } J_{\text{CF}} = 245.1 \text{ Hz}, C_{\text{Ar}}\text{-F}), \text{ 131.9 (d, } ^{3}J_{\text{CP}} = 16.3 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 14.1 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 14.1 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 14.1 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 14.1 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 14.1 \text{ Hz}, \text{P-CH-CH=CH}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 131.7 (d, } ^{3}J_{\text{CP}} = 16.1 \text{ Hz}, \text{ CH}_{\text{CH}}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{dipp}}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{CH}_{\text{cH}}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{ CH}_{\text{cH}}), \text{ 130.8 (s, CH_{\text{Ph}} \text{ and } \text{ and$ 128.3 (CH<sub>Ph</sub>), 128.2 (CH<sub>Ph</sub>), 125.8 (d,  $J_{CP} = 12.5$  Hz, C=C(Ph)<sub>2</sub>), 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, <sup>1</sup>J<sub>CP</sub> = 89.7 Hz, C-P), 53.5 (d, C<sub>tBu</sub> overlapped by deuterated solvant), 53.4 (d,  $C_{tBu}$  overlapped by deuterated solvant), 51.9 (d,  ${}^{2}J_{CP} = 11.6$  Hz,  $CH_{bridgehead}$ ), 49.1 (d,  ${}^{2}J_{CP}$  = 8.6 Hz,  $CH_{bridgehead}$ ), 47.3 (d,  ${}^{2}J_{CP}$  = 61.5 Hz, P-CH), 43.8 (s, CH<sub>2</sub>), 32.3 (d, 2 CH<sub>3tBu</sub> overlapped), 28.4 (s, CH<sub>iPr</sub>), 28.0 (s, CH<sub>2</sub>), 27.9 (s, CH<sub>iPr</sub>), 26.9 (s, CH<sub>2</sub>), 25.3 (s, CH<sub>3iPr</sub>), 25.0 (s,  $CH_{3iPr}$ ), 24.9 (s,  $CH_{3iPr}$ ), 24.7 (s,  $CH_{3iPr}$ ), 4.7 (s,  $Si-CH_3$ ), 3.6 (d,  ${}^{3}J_{CP} = 2.9$  Hz, Si-CH<sub>3</sub>), 2.8 (s, SiH-CH<sub>3</sub>), -3.4 (s, SiH-CH<sub>3</sub>).

<sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  49.3 (s). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -132.8 (br, C<sub>Ar</sub>-F<sub>ortho</sub>), -163.5 (t, J<sub>FF</sub> = 20.4 Hz, C<sub>Ar</sub>-F<sub>para</sub>), -167.3 (t, J<sub>FF</sub> = 18.0 Hz, C<sub>Ar</sub>-F<sub>meta</sub>). <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  -16.9 (s, BAr). <sup>29</sup>Si NMR (80 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  22.3 (d, <sup>2</sup>J<sub>SiF</sub> = 4.5 Hz, SiMe<sub>2</sub>), -3.7 (s, SiMe<sub>2</sub>H). Synthesis of 4b (R<sup>2</sup> = R<sup>3</sup> = 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 it was stirred for 10 min, the solution was filtered then the solvents were 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. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.45–7.24 (m, 3H, CH<sub>dipp</sub>), 3.39 (s, 1H, CH<sub>bridgehead</sub>), 2.96 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 2.83 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H, CH<sub>iPr</sub>), 2.71 (s, 1H, CH<sub>bridgehead</sub>), 2.06–1.83 (m, 2H, CH<sub>2</sub>), 1.81– 1.66 (m, 2H,  $CH_2$ ), 1.61–1.52 (m, 2H,  $CH_2$ ), 1.40 (s, 9H,  $CH_{3tBu}$ ), 1.37 (s, 9H,  $CH_{3tBu}$ ), 1.29 (d,  ${}^{3}J_{HH}$  = 4.0 Hz, 3H,  $CH_{3iPr}$ ), 1.26 (d,  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, 3\text{H}, CH_{3iPr}$ , 1.18 (d,  ${}^{3}J_{\text{HH}} = 4.0 \text{ Hz}, 3\text{H}, CH_{3iPr}$ ), 1.16  $(d, {}^{3}J_{HH} = 6.7 \text{ Hz}, 3H, CH_{3iPr}), 0.82 (d, {}^{3}J_{HP} = 6.6 \text{ Hz}, 3H, Si^{+}-CH_{3}),$ 0.77 (s, 3H, Si–CH<sub>3</sub>), 0.69 (d,  ${}^{3}J_{\text{HP}}$  = 6.4 Hz, 3H, Si<sup>+</sup>–CH<sub>3</sub>), 0.65 (s, 3H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  192.3 (d, <sup>2</sup>J<sub>CP</sub>= 25.9 Hz, N-C), 148.6 (br d,  $J_{CF}$  = 241.3 Hz,  $C_{Ar}$ -F), 147.5 (s,  $C_{dipp}$ ), 147.3 (s,  $C_{dipp}$ ), 138.6 (br d,  $J_{CF}$  = 244.8 Hz,  $C_{Ar}$ -F), 136.7 (br d,  $J_{CF}$ = 245.8 Hz,  $C_{\rm Ar}$ -F), 132.1 (d,  ${}^{3}J_{\rm CP}$  = 3.1 Hz, N- $C_{\rm dipp}$ ), 129.9 (s, CH<sub>dipp</sub>), 125.8 (s, CH<sub>dipp</sub>), 125.7 (s, CH<sub>dipp</sub>), 99.0 (d,  ${}^{1}J_{CP} = 68.9$  Hz, C-P), 53.3 (d,  ${}^{2}J_{CP} = 21.2$  Hz, C<sub>tBu</sub>), 53.2 (d,  ${}^{2}J_{CP} = 19.4$  Hz, C<sub>tBu</sub>), 48.7 (d,  ${}^{3}J_{CP} = 6.0$  Hz, CH<sub>2</sub>), 45.0 (d,  ${}^{2}J_{CP} = 10.5$  Hz, CH<sub>bridgehead</sub>), 41.5 (s, CH<sub>bridgehead</sub>), 32.9 (d,  ${}^{3}J_{CP} = 5.6$  Hz, CH<sub>3tBu</sub>), 32.6 (d,  ${}^{3}J_{CP} = 5.6$  Hz, CH<sub>2</sub>), 28.5 (a, CH<sub>2</sub>), 28.4 (a, CH<sub>2</sub>), 28.4 (a, CH<sub>2</sub>), 28.4 (b, CH<sub>2</sub>), 28.4 (b 5.6 Hz, CH<sub>3tBu</sub>), 28.5 (s, CH<sub>iPr</sub>), 28.4 (s, CH<sub>iPr</sub>), 28.1 (s, CH<sub>2</sub>), 26.1 (s,  $CH_{3iPr}$ ), 25.7 (d,  ${}^{3}J_{CP}$  = 1.8 Hz,  $CH_{2}$ ), 25.3 (s,  $CH_{3iPr}$ ), 24.5 (s,  $CH_{3iPr}$ ), 24.4 (s,  $CH_{3iPr}$ ), 6.1 (s,  $Si-CH_3$ ), 4.3 (d,  ${}^{3}J_{CP} = 1.8$  Hz, Si- $CH_3$ ), 1.4 (d,  ${}^{2}J_{CP}$  = 14.2 Hz, Si<sup>+</sup> $-CH_3$ ), 0.7 (d,  ${}^{2}J_{CP}$  = 13.4 Hz, Si<sup>+</sup>-CH<sub>3</sub>).  $C_{ipso}$  attached to the boron atom could not be detected. <sup>31</sup>P NMR (121 MHz,  $CD_2Cl_2$ ):  $\delta$  39.6 (<sup>1</sup> $J_{PSi}$  = 132 Hz). <sup>11</sup>B NMR (96 MHz,  $CD_2Cl_2$ ):  $\delta - 16.6$  (s, BAr). <sup>19</sup>F NMR (282 MHz,  $CD_2Cl_2$ ):  $\delta$ -133.0 (br,  $C_{Ar}-F_{ortho}$ ), -163.7 (t,  $J_{FF} = 20.3$  Hz,  $C_{Ar}-F_{para}$ ), -167.5(t,  $J_{FF} = 18.3 \text{ Hz}$ ,  $C_{Ar} - F_{meta}$ ). <sup>29</sup>Si NMR (60 MHz,  $CD_2Cl_2$ ):  $\delta$  21.4 (d,  ${}^{2}J_{SiP} = 2.9$  Hz,  $SiMe_{2}$ ), 6.1 (d,  ${}^{1}J_{SiP} = 132.0$  Hz,  $Si^{+}$ ). Anal. Calcd for C55H55BF20N3PSi2: C, 53.45; H, 4.49; N, 3.40. Found: C, 53.21; H, 4.43; N, 3.38. Mp: 86.1 °C.

Synthesis of 4c ( $R^2 = Me$ ;  $R^3 = Cl$ ). 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 was obtained. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.47-7.40 (m, 2H, CH<sub>dipp</sub>), 7.35–7.26 (m, 4H, CH<sub>dipp</sub>), 3.43 (s, 2H,  $CH_{bridgehead}$ ), 3.07 (sept,  ${}^{3}J_{HH} = 6.6$  Hz, 1H,  $CH_{iPr}$ ), 2.91 (sept,  ${}^{3}J_{HH}$ = 6.9 Hz, 1H,  $CH_{iPr}$  overlapped with  $CH_{iPr}$ ), 2.89 (sept,  ${}^{3}J_{HH}$  = 6.9 Hz, 1H, CH<sub>iPr</sub> overlapped with CH<sub>iPr</sub>), 2.83-2.70 (br, 1H, CH<sub>iPr</sub> overlapped by  $CH_{bridgehead}$ ), 2.83–2.70 (br, 2H,  $CH_{bridgehead}$  overlapped by  $CH_{iPr}$ ), 2.05–1.89 (m, 4H,  $CH_2$ ), 1.81–1.66 (m, 4H,  $CH_2$ ), 1.64–1.56 (m, 2H,  $CH_2$ ), 1.45 (d,  ${}^{4}J_{PH}$  = 0.88 Hz, 9H,  $CH_{3tBu}$ ), 1.44 (d,  ${}^{4}J_{PH} = 0.87$  Hz, 3H,  $CH_{3tBu}$ ), 1.40 (d,  ${}^{4}J_{PH} = 0.98$  Hz, 3H,  $CH_{3tBu}$ ), 140–1.36 (m, 2H, CH<sub>2</sub>), 1.38 (d,  ${}^{4}J_{PH}$  = 0.94 Hz, 3H, CH<sub>3tBu</sub>), 1.32– 1.26 (m, 12H, CH<sub>3iPr</sub>), 1.21-1.14 (m, 12H, CH<sub>3iPr</sub> overlapped by  $Si^+-CH_3$ , 1.21–1.14 (d,  ${}^{3}J_{PH}$  = 4.1 Hz\*, 3H,  $Si^+-CH_3$  overlapped by  $CH_{3iPr}$ ), 1.03 (d,  ${}^{3}J_{PH}$  = 4.1 Hz, 3H, Si<sup>+</sup>-CH<sub>3</sub>), 0.81 (d,  ${}^{2}J_{PH}$  = 2.2 Hz, 6H, Si-CH<sub>3</sub>), 0.70 (d,  ${}^{2}J_{PH}$  = 2.5 Hz, 6H, Si-CH<sub>3</sub>). \* coupling constant determined by HSQC <sup>29</sup>Si-<sup>1</sup>H. <sup>13</sup>C NMR (101 MHz,  $CD_2Cl_2$ ):  $\delta$  192.4 (d,  ${}^2J_{CP}$  = 23.2 Hz, N–C), 192.3 (d,  ${}^2J_{CP}$  = 23.2 Hz, N-C), 148.6 (br d,  $J_{CF}$  = 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,  $J_{CF}$  = 245.1 Hz,  $C_{Ar}$ -F), 136.7 (br d,  $J_{CF}$  = 246.4 Hz,  $C_{Ar}$ -F), 130.7 (d,  ${}^{3}J_{CP}$  = 2.8 Hz, N- $C_{dipp}$ ), 130.6 (d,  ${}^{3}J_{CP}$  = 2.6 Hz, N- $C_{dipp}$ ), 130.4 (s,  $CH_{dipp}$ ), 130.4 (s,  $CH_{dipp}$ ), 130.7 (d) (s, CH<sub>dipp</sub>), 126.3 (s, CH<sub>dipp</sub>), 126.2 (s, CH<sub>dipp</sub>), 125.8 (s, CH<sub>dipp</sub>), 125.7 (s,  $CH_{dipp}$ ), 124.4 (broad s,  $B-C_{Ar}$ ), 99.3 (d,  ${}^{1}J_{CP}$  = 74.6 Hz, C-P), 99.2 (d,  ${}^{1}J_{CP}$  = 72.8 Hz, C-P), 54.4 (d,  $C_{tBu}$  overlapped by deuterated solvant), 54.2 (d,  ${}^{2}J_{CP} = 1.5$  Hz,  $C_{tBu}$ ), 53.7 (d,  ${}^{2}J_{CP} = 1.2$ Hz,  $C_{tBu}$ ), 53.5 (d,  ${}^{2}J_{CP} = 1.2$  Hz,  $C_{tBu}$ ), 48.9 (d,  ${}^{3}J_{CP} = 6.7$  Hz,  $CH_{2}$ ), 48.4 (d,  ${}^{3}J_{CP} = 6.1$  Hz,  $CH_{2}$ ), 45.3 (s,  $CH_{bridgehead}$ ), 45.2 (s,  $CH_{bridgehead}$ ), 41.8 (s,  $CH_{bridgehead}$ ), 41.6 (s,  $CH_{bridgehead}$ ), 32.8 (d,  $^{3}J_{CP}$ 

= 5.6 Hz, 2 CH<sub>3tBu</sub>), 32.5 (d, <sup>3</sup>*J*<sub>CP</sub> = 5.8 Hz, CH<sub>3tBu</sub>), 32.4 (d, <sup>3</sup>*J*<sub>CP</sub> = 5.6 Hz, CH<sub>3tBu</sub>), 28.8 (s, CH<sub>iPr</sub>), 28.7 (s, CH<sub>iPr</sub>), 28.6 (s, CH<sub>iPr</sub>), 28.5 (s, CH<sub>iPr</sub>), 27.9 (s, CH<sub>2</sub>), 27.6 (s, CH<sub>2</sub>), 26.1 (s, CH<sub>3iPr</sub>), 25.7 (s, CH<sub>3iPr</sub>), 25.5 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.8 Hz, CH<sub>2</sub>), 25.5 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.8 Hz, CH<sub>2</sub>), 25.5 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.8 Hz, CH<sub>2</sub>), 25.3 (s, CH<sub>3iPr</sub>), 25.1 (s, CH<sub>3iPr</sub>), 25.0 (s, CH<sub>3iPr</sub>), 24.9 (s, CH<sub>3iPr</sub>), 24.4 (s, CH<sub>3iPr</sub>), 24.3 (s, CH<sub>3iPr</sub>), 6.0 (s, Si-CH<sub>3</sub>), 5.9 (s, 2 Si-CH<sub>3</sub>), 4.4 (d, <sup>2</sup>*J*<sub>CP</sub> = 18.9 Hz, Si<sup>+</sup>-CH<sub>3</sub>), 4.3 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.7 Hz, Si-CH<sub>3</sub>), 4.2 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.7 Hz, Si-CH<sub>3</sub>), 3.7 (d, <sup>2</sup>*J*<sub>CP</sub> = 18.0 Hz, Si<sup>+</sup>-CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 30.2 (<sup>1</sup>*J*<sub>PSi</sub> = 172.6 Hz), 30.0 (<sup>1</sup>*J*<sub>PSi</sub> = 171.2 Hz). <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -16.6 (s, BAr). <sup>19</sup>F NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -132.5 (br, C<sub>Ar</sub>-*F<sub>ortho</sub>*), -163.3 (t, *J*<sub>FF</sub> = 20.5 Hz, C<sub>Ar</sub>-*F<sub>paral</sub>*), -167.0 (t, *J*<sub>FF</sub> = 19.3 Hz, *Si*Me<sub>2</sub>), 23.8 (d, <sup>2</sup>*J*<sub>SIP</sub> = 2.7 Hz, SiMe<sub>2</sub>), -0.3 (d, <sup>1</sup>*J*<sub>SiP</sub> = 172.6 Hz, Si<sup>+</sup>), -2.1 (d, <sup>1</sup>*J*<sub>SiP</sub> = 171.2 Hz, Si<sup>+</sup>). Mp: 157.7 °C.

Synthesis of 4d ( $R^2 = CI; R^3 = H$ ). White powder (0.511 g, 82%). Crystals suitable for X-ray diffraction analysis were obtained from a concentrated chloroform solution. A single diastereomer was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49-7.43 (m, 1H,  $CH_{dipp}$ ), 7.33–7.28 (m, 2H,  $CH_{dipp}$ ), 5.90 (d, 1H,  ${}^{2}J_{PH}$  = 58.4 Hz, SiH), 3.45 (s,1H, CH<sub>bridgehead</sub>), 2.96 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H, CH<sub>iPr</sub>), 2.87 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H, CH<sub>iPr</sub> overlapped by CH<sub>bridgehead</sub>), 2.83 (s, 1H,  $CH_{bridgehead}$  overlapped by  $CH_{iPr}$ ), 2.07–1.93 (m, 2H,  $CH_2$ ), (c) (1) Orbiggeneral of  $A_{\rm HP}$  (2) (1.32 - 1.60) (m, 4H, 2  $CH_2$ ), 1.43 (d, 9H,  ${}^4J_{\rm PH}$  = 0.8 Hz,  $CH_{3\rm IBu}$ ), 1.24 (d, 9H,  ${}^4J_{\rm PH}$  = 0.8 Hz,  $CH_{3\rm IBu}$ ), 1.29 (d, 3H,  ${}^3J_{\rm HH}$  = 6.8 Hz,  $CH_{3\rm IPr}$ ), 1.27 (d, 3H,  ${}^3J_{\rm HH}$  = 6.8 Hz,  $CH_{3\rm IPr}$ ), 1.24 (d, 6H,  ${}^3J_{\rm HH}$  = 6.8 Hz, 2  $CH_{3\rm IPr}$ ), 0.80 (s, 3H, SiMe<sub>2</sub>), 0.72 (s, 3H, SiMe<sub>2</sub>).  ${}^{13}C$  NMR (101  $M_{\rm HP}$ ), 0.80 (s) (d)  $M_{\rm HP}$  = 0.8  $M_{\rm HP}$  (d)  $M_{\rm HP}$  (d) MHz, CDCl<sub>3</sub>):  $\delta$  192.3 (d, <sup>2</sup>J<sub>CP</sub>= 22.2 Hz, N–C), 148.2 (br d, J<sub>CF</sub> = 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,  ${}^{1}J_{CP}$  = 76.7 Hz, C-P), 53.5 (br,  $C_{tBu}$ ), 53.4 (br,  $C_{tBu}$ ), 48.3 (d,  $J_{CP}$  = 6.4 Hz, CH<sub>2</sub>), 44.8 (d,  ${}^{3}J_{CP} = 10.0$  Hz, CH<sub>bridgehead</sub>), 41.6 (s, CH<sub>bridgehead</sub>), 32.6 (d,  ${}^{3}J_{CP} = 5.8$  Hz, CH<sub>3tBu</sub>), 32.4 (d,  ${}^{3}J_{CP} = 5.8$  Hz, CH<sub>3tBu</sub>), 28.8 (s,  $CH_{iPr}$ ), 28.6 (s,  $CH_{iPr}$ ), 27.6 (s,  $CH_2$ ), 25.1 (s,  $CH_{3iPr}$ ), 24.8 (d,  $J_{CP}$  = 1.7 Hz, CH<sub>2</sub>), 24.7 (s, CH<sub>3iPr</sub>), 24.5 (s, CH<sub>3iPr</sub>), 24.2 (s, CH<sub>3iPr</sub>), 5.1 (s, SiMe<sub>2</sub>), 3.9 (d,  ${}^{3}J_{CP} = 1.7$  Hz, SiMe<sub>2</sub>).  $C_{ipso}$  attached to the boron atom could not be detected.  ${}^{31}P$  NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  28.2  $({}^{1}J_{SiP} = 169.1 \text{ Hz}, {}^{2}J_{PH} = 58.5 \text{ Hz}). {}^{11}B \text{ NMR} (160 \text{ MHz}, \text{CDCl}_3): \delta$ -16.6 (s, BAr). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>):  $\delta$  -132.5 (br, C<sub>Ar</sub>- $F_{ortho}$ ), -163.3 (t,  $J_{FF}$  = 20.5 Hz,  $C_{Ar}F_{para}$ ), -167.0 (t,  $J_{FF}$  = 19.3 Hz,  $C_{Ar}-F_{meta}$ ). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>):  $\delta$  24.0 (s, SiMe<sub>2</sub>), -23.3 (d,  ${}^{1}J_{\text{SiP}} = 169.1 \text{ Hz}, Si^{+}$ ). Mp: 150.3 °C.

Synthesis of 4e ( $R^2 = R^3 = CI$ ). White powder (0.466 g, 77%). Crystals suitable for X-ray diffraction analysis were obtained from a concentrated chloroform solution. <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$ 7.54–7.24 (m, 3H,  $CH_{dipp}$ ), 3.48 (s, 1H,  $CH_{bridgehead}$ ), 3.01 (sept, <sup>3</sup> $J_{HH}$ = 6.8 Hz, 1H,  $CH_{iPr}$ ), 2.93–2.77 (sept,  ${}^{3}J_{HH}$  = 6.7 Hz, 1H,  $CH_{iPr}$ overlapped by CH<sub>bridgehead</sub>), 2.88-2.77 (s,1H, CH<sub>bridgehead</sub> overlapped by CH<sub>iPr</sub>), 2.12- 1.55 (m, 2H, CH<sub>2</sub>), 2.12- 1.55 (m, 2H, CH<sub>2</sub>), 2.12-1.55 (m, 2H, CH<sub>2</sub>), 1.46 (s, 9H, CH<sub>3tBu</sub>), 1.45 (s, 9H, CH<sub>3tBu</sub>),1.33 (d, 3H,  ${}^{3}J_{HH} = 5.5$  Hz,  $CH_{3iPr}$ ), 1.31 (d, 3H,  ${}^{3}J_{HH} = 5.5$  Hz,  $CH_{3iPr}$ ), 0.80 (d, 6H,  ${}^{3}J_{HH} = 6.7$  Hz,  $CH_{3iPr}$ ), 0.85 (s, 3H, SiMe<sub>2</sub>), 0.75 (s, 3H, SiMe<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  191.7 (d, <sup>2</sup>J<sub>CP</sub> = 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,  $C_{\text{dipp}}$ ), 138.3 (br d,  $J_{\text{CF}}$  = 245.5 Hz,  $C_{\text{Ar}}$ -F), 136.3 (br d,  $J_{\text{CF}}$  = 247.4 Hz,  $C_{Ar}$ -F), 130.3 (s, CH<sub>dipp</sub>), 129.0 (br, N- $C_{dipp}$ ), 125.8 (s, CH<sub>dipp</sub>), 125.7 (s, CH<sub>dipp</sub>), 98.6 (d, <sup>1</sup> $J_{CP}$  = 80.1 Hz, C-P), 54.3 (d, <sup>3</sup> $J_{CP}$  = 1.9 Hz,  $C_{tBu}$ ), 54.1 (d,  $C_{tBu}$  overlapped by deuterated solvent), 47.9 (d,  $J_{CP}$ = 6.8 Hz,  $CH_2$ ), 45.3 (d,  ${}^{2}J_{CP}$  = 9.6 Hz,  $CH_{bridgehead}$ ), 41.6 (d,  ${}^{3}J_{CP}$  = 1.2 Hz,  $CH_{bridgehead}$ ), 32.4 (d,  ${}^{3}J_{CP}$  = 5.9 Hz,  $CH_{3tBu}$ ), 31.9 (d,  ${}^{3}J_{CP}$  = 5.9 Hz,  $CH_{3tBu}$ , 28.4 (s,  $CH_{iPr}$ ), 28.3 (s,  $CH_{iPr}$ ), 27.1 (s,  $CH_2$ ), 25.3 (s,  $CH_{3iPr}$ ), 24.9 (d,  $J_{CP}$  = 1.9 Hz,  $CH_2$ ), 24.6 (s,  $CH_{3iPr}$ ), 24.4 (s,  $CH_{3iPr}$ ), 24.3 (s,  $CH_{3iPr}$ ), 5.3 (s,  $SiMe_2$ ), 3.7 (d,  ${}^{3}J_{CP} = 1.4 Hz$ ,  $SiMe_2$ ). C<sub>ipso</sub> attached to the boron atom could not be detected. <sup>31</sup>P NMR (121 MHz,  $CD_2Cl_2$ ):  $\delta$  21.8 ( ${}^1J_{SiP}$  = 237.4 Hz).  ${}^{11}B$  NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -16.6 (s, BAr). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -133.0 (br, C- $F_{ortho}$ ), -163.7 (t,  $J_{FF}$  = 20.3 Hz,  $C_{Ar}-F_{para}$ ), -167.5 (t,  $J_{FF}$  = 18.3 Hz,  $C_{Ar} - F_{meta}$ ). <sup>29</sup>Si NMR (60 MHz,  $CD_2Cl_2$ ):  $\delta$  25.6 (d, <sup>2</sup> $J_{SiP}$  = 2.88 Hz,  $SiMe_2$ ), -21.6 (d,  ${}^{1}J_{SiP}$  = 237.4 Hz,  $Si^+$ ). Anal. Calcd for  $C_{53}H_{49}BCl_2F_{20}N_3PSi_2:$  C, 49.86; H, 3.87; N, 3.29. Found: C, 49.79; H, 3.83; N, 3.35. Mp: 189.4  $^{\circ}C.$ 

Synthesis of 5f ( $\mathbf{R}^2 = \mathbf{R}^3 = \mathbf{Me}$ ). 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 it was stirred for 10 min, the solution was filtered and all the volatiles were removed under vacuum to give 5f as a white powder (213 mg, 72%). <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  7.83–7.56 (m, 10H,  $P(C_6H_5)_2$ ), 7.45–7.20 (m, 3H,  $CH_{dipp}$ ), 3.55 (s, 1H,  $CH_{bridgehead}$ ), 3.06 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 2.79 (s, 1H,  $CH_{bridgehead}$ ), 2.66 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H,  $CH_{iPr}$ ), 2.10–1.91 (m, 2 + 1H,  $CH_2$ ), 1.67–1.58 (m, 1H,  $CH_2$ ), 1.53–1.41 (m, 2H, CH<sub>2</sub>), 1.28 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 3H, CH<sub>3iPr</sub>), 1.26 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 3H,  $CH_{3iPr}$ ), 1.14 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 3H,  $CH_{3iPr}$ ), (a)  $J_{\text{HH}} = 6.8 \text{ Hz}, 3H, CH_{3iPr}$ ) H1 (a)  $J_{\text{HH}} = 6.6 \text{ Hz}, 3H, CH_{3iPr}$ ) 1.06 (d,  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, 3H, CH_{3iPr}$ ), 0.81 (d,  ${}^{3}J_{\text{PH}} = 6.6 \text{ Hz}, 3H, Si-CH_{3}$ ), 0.51 (d,  ${}^{3}J_{\text{PH}} = 6.6 \text{ Hz}, 3H, Si-CH_{3}$ ). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  187.5 (d,  ${}^{2}J_{\text{CP}} = 16.4 \text{ Hz}, \text{N-C}$ ), 148.7 (br d,  $J_{\text{CF}} = 241.3$ 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<sub>ph</sub>), 134.4 (d,  $J_{CP}$  = 3.4 Hz, CH<sub>ph</sub>), 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<sub>Ph</sub>), 130.0 (s, CH<sub>dipp</sub>), 125.8 (s, CH<sub>dipp</sub>), 125.7 (s, CH<sub>dipp</sub>), 121.7  $(d, {}^{1}J_{CP} = 70.3 \text{ Hz}, P - C_{Ph}), 119.5 (d, {}^{1}J_{CP} = 74.0 \text{ Hz}, P - C_{Ph}), 86.7 (d, )$  ${}^{1}J_{CP}$  = 73.2 Hz, C-P), 49.3 (d,  ${}^{3}J_{CP}$  = 5.0 Hz, CH<sub>2</sub>), 45.1 (d,  ${}^{2}J_{CP}$  = 8.9 Hz,  $CH_{bridgehead}$ ), 42.8 (d,  ${}^{3}J_{CP}$  = 1.0 Hz,  $CH_{bridgehead}$ ), 29.1 (s,  $CH_{2}$ ), 28.7 (s,  $CH_{iPr}$ ), 28.6 (s,  $CH_{iPr}$ ), 26.4 (d,  ${}^{3}J_{CP} = 2.1$  Hz,  $CH_{2}$ ), 25.6 (s,  $CH_{3iPr}$ ), 25.4 (s,  $CH_{3iPr}$ ), 24.9 (s,  $CH_{3iPr}$ ), 23.6 (s,  $CH_{3iPr}$ ), -0.33 (d,  ${}^{2}J_{CP} = 15.0 \text{ Hz}, \text{ Si}^{+}-CH_{3}), -3.0 \text{ (d, } {}^{2}J_{CP} = 11.0 \text{ Hz}, \text{ Si}^{+}-CH_{3}). C_{ipso}$ attached to the boron atom could not be detected. <sup>31</sup>P NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -20.8 (<sup>1</sup>J<sub>PSi</sub> = 82.1 Hz). <sup>19</sup>F NMR (282 MHz,  $CD_2Cl_2$ :  $\delta$  -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,  $C_{Ar}$ - $F_{meta}$ ). <sup>11</sup>B NMR (96 MHz,  $CD_2Cl_2$ ):  $\delta - 16.6$  (s, BAr). <sup>29</sup>Si NMR (60 MHz,  $CD_2Cl_2$ ):  $\delta 27.2$  (d,  $^{1}J_{PSi} = 82.1 \text{ Hz}$ ). Mp: 84.6 °C.

Synthesis of 5g ( $R^2 = CI$ ;  $R^3 = Me$ ). 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 it was stirred for 10 min, the solution was filtered by cannula and evaporated under vacuum to give 5g as a white powder (484 mg, 76%). Data for the major isomer (76%) are as follows. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ):  $\delta$  7.89–7.60 (m, 10H,  $P(C_6H_5)_2$ ), 7.48–7.39 (m, 1H, CH<sub>dipp</sub>), 7.37-7.29 (m, 1H, CH<sub>dipp</sub>), 7.24-7.19 (m, 1H, CH<sub>dipp</sub>), 3.58 (s, 1H,  $CH_{bridgehead}$ ), 3.28 (sept,  ${}^{3}J_{HH} = 6.8$  Hz, 1H,  $CH_{iPr}$ ), 2.83 (s, 1H,  $CH_{bridgehead}$ ), 2.46 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 2.11- 1.91 (m, 2H,  $CH_2$ ), 1.68–1.34 (m, 4H, 2  $CH_2$ ), 1.28 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 3H,  $CH_{3iPr}$ ), 1.27 (d,  ${}^{3}J_{HH}$  = 6.7 Hz, 3H,  $CH_{3iPr}$ ), 1.08 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 3H,  $CH_{3iPr}$ ), 0.94 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 3H,  $CH_{3iPr}$ ), 0.83 (d,  ${}^{3}J_{PH}$  = 4.3 Hz, 3H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz,  $CD_2Cl_2$ ):  $\delta$  185.9 (d,  ${}^{2}J_{CP}$  = 13.1 Hz, N–C), 148.6 (br d,  $J_{CF}$  = 241.7 Hz,  $C_{Ar}$ –F), 148.4 (s,  $C_{\text{dipp}}$ ), 147.5 (s,  $C_{\text{dipp}}$ ), 138.7 (br d,  $J_{\text{CF}}$  = 243.8 Hz,  $C_{\text{Ar}}$ -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<sub>Ph</sub>), 130.5 (s, CH<sub>dipp</sub>), 126.2 (s, CH<sub>dipp</sub>), 125.6 (s, CH<sub>dipp</sub>), 124.5 (br, B- $C_{Ar}$ ), 119.5 (d,  ${}^{1}J_{CP}$  = 72.5 Hz, P- $C_{Ph}$ ), 116.4 (d,  ${}^{1}J_{CP}$  = 77.5 Hz, P- $C_{\text{Ph}}$ ), 89.2 (d,  ${}^{1}J_{\text{CP}}$  = 74.6 Hz, C-P), 49.1 (d,  ${}^{3}J_{\text{CP}}$  = 5.5 Hz, CH<sub>2</sub>), 45.4 (d,  ${}^{2}J_{CP} = 8.5$  Hz, CH<sub>bridgehead</sub>), 43.1 (d,  ${}^{3}J_{CP} = 1.8$  Hz, CH<sub>bridgehead</sub>), 29.0 (s, 2 CH<sub>iPr</sub>), 28.8 (s, CH<sub>2</sub>), 26.1 (d,  ${}^{3}J_{C} = 2.3$  Hz,  $CH_2$ ), 25.5 (s,  $CH_{3iPr}$ ), 25.5 (s,  $CH_{3iPr}$ ), 24.8 (s,  $CH_{3iPr}$ ), 23.1 (s,  $CH_{3iPr}$ ), 0.0 (d,  ${}^{2}J_{CP}$  = 15.1 Hz, Si<sup>+</sup> $-CH_{3}$ ). C<sub>ipso</sub> attached to the boron atom could not be detected. <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -24.3  $({}^{1}J_{PSi} = 124.6 \text{ Hz})$ .  ${}^{19}F$  NMR (471 MHz,  $CD_{2}Cl_{2}$ ):  $\delta$  -133.0 (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,  $C_{Ar} - F_{meta}$ ). <sup>11</sup>B NMR (160 MHz,  $CD_2Cl_2$ ):  $\delta$  –16.6 (s, BAr). <sup>29</sup>Si NMR (99 MHz,  $CD_2Cl_2$ ):  $\delta$  15.4 (d,  ${}^{1}J_{PSi}$  = 124.6 Hz). Mp: 78.8 °C. Data for the minor isomer (24%) are as follows. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.89–7.59 (m, 10H, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>\*), 7.48–7.39 (m, 1H, CH<sub>dipp</sub>\*), 7.37–7.29 (m, 1H, CH<sub>dipp</sub>\*), 7.24–7.19 (m, 1H, CH<sub>dipp</sub>\*), 3.58 (s, 1H,  $CH_{bridgehead}^*$ ), 2.98 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ),

2.89-2.79 (br, 1H, CH<sub>iPr</sub>\*), 2.89-2.79 (br, 1H, CH<sub>bridgehead</sub>\*), 2.11-1.91 (m, 2H,  $CH_2^*$ ), 1.68–1.34 (m, 4H, 2  $CH_2^*$ ), 1.31 (d,  ${}^{3}J_{HH} = 6.7$ Hz, 3H,  $CH_{3iPr}$ ), 1.26 (d, 3H,  $CH_{3iPr}^*$ ), 1.20 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 3H,  $CH_{3iPr}$ ), 1.18 (d,  ${}^{3}J_{PH}$  = 4.4 Hz, 3H, Si– $CH_{3}$  overlapped with  $CH_{3iPr}$ ), 1.17 (d,  ${}^{3}J_{HH}$  = 7.0 Hz, 3H,  $CH_{3iPr}$  overlapped with Si– $CH_{3}$ ). <sup>13</sup>C NMR (126 MHz,  $CD_2Cl_2$ ):  $\delta$  187.3 (d,  ${}^2J_{CP}$  = 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,  $(H_{Ph}^{*})$ , 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,  ${}^{1}J_{CP}$  = 76.4 Hz,  $P-C_{Ph}$ ), 118.3 ( $d_{r}^{11}J_{CP} = 75.2 \text{ Hz}, P-C_{Ph}$ ), 87.0 ( $d_{r}^{11}J_{CP} = 73.7 \text{ Hz}, C-P$ ), 49.1 (d,  $CH_2^*$ ), 45.5 (d,  ${}^{2}J_{CP}$  = 8.8 Hz,  $CH_{bridgehead}$ ), 42.8 (s,  $CH_{bridgehead}$ ), 28.9 (s, 2  $CH_{iPr}$ ), 28.5 (s,  $CH_2$ ), 26.5 (d,  ${}^{3}J_{C}$  = 2.5 Hz,  $CH_2$ ), 25.8 (s,  $CH_{3iPr}$ ), 25.3 (s,  $CH_{3iPr}$ ), 24.6 (s,  $CH_{3iPr}$ ), 24.4 (s,  $CH_{3iPr}$ ), 2.9 (d,  ${}^{2}J_{CP}$  = 17.8 Hz,  $Si^+$ - $CH_3$ ).  ${}^{31}P$  NMR (202 MHz,  $CD_2Cl_2$ ):  $\delta$  –24.1 ( ${}^{1}J_{PSi}$  = 117.4). <sup>19</sup>F NMR (471 MHz,  $CD_2Cl_2$ ):  $\delta$  -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,  $C_{Ar} - F_{para}$ )  $F_{meta}$ ). <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –16.6 (s, BAr). <sup>29</sup>Si NMR (99 MHz,  $CD_2Cl_2$ ):  $\delta$  15.3 (d,  ${}^{1}J_{PSi}$  = 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  $\mu$ L, 0.042 mmol), and then the solution was warmed at 50 °C for 4 h. Then the solution was evaporated under vacuum and the resulting crude product was washed with  $3 \times 0.3$  mL of pentane. Product 6 was isolated as a white powder in 60% yield (32 mg). <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ):  $\delta$  7.83–7.53 (m, 8H,  $P(C_6H_5)_2$ ), 7.43– 7.36 (m, 1H,  $CH_{dipp}$ ), 7.32–7.25 (m, 2H,  $CH_{dipp}$  overlapped by  $P(C_6H_5)_2))$ , 7.32–7.25 (m, 2H,  $P(C_6H_5)_2$  overlapped by  $CH_{dipp})$ , 3.94 (ddd, 1H,  ${}^{3}J_{PH} = 25.3 \text{ Hz}$ ,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ ,  ${}^{3}J_{HH} = 3.2 \text{ Hz}$ ,  $CH = C_{12}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 3.2 \text{ Hz}$ ,  $CH = C_{12}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 3.2 \text{ Hz}$ ,  $CH = C_{12}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 3.2 \text{ Hz}$ ,  $CH = C_{12}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ ,  $CH = C_{12}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 14.3 Hz,  ${}^{3}J_{HH} = 6.2 \text{ Hz}$ , CH = 12.3 Hz, CH = 12P-CH<sub>2</sub>), 3.44 (s, 3H, O-CH<sub>3</sub>), 3.41 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H,  $(H_{\rm iPr})$ , 3.11 (sept,  ${}^{3}J_{\rm HH}$  = 6.8 Hz, 1H,  $(H_{\rm iPr})$ , 2.93 (br, 1H,  $(H_{\rm iPr})$ , 2.49 (br, 1H,  $(H_{\rm bridgehead})$ , 1.99–1.90 (m, 1H,  $(H_{\rm 2})$ , 1.80–1.52 (m, 3H,  $(H_{2})$ , 1.48–1.41 (m, 1H,  $(H_{2})$ , 1.38 (d,  ${}^{3}J_{\rm PH}$  = 6.9 Hz, 3H,  $CH_{3iPr}$ ), 1.31 (d,  ${}^{3}J_{PH}$  = 6.8 Hz, 3H,  $CH_{3iPr}$ ), 1.27 (d,  ${}^{3}J_{PH}$ = 6.9 Hz, 3H,  $CH_{3iPr}$ ), 1.24 (d,  ${}^{3}J_{PH}$  = 6.8 Hz, 3H,  $CH_{3iPr}$ ), 1.11–1.07 (m, 1H,  $CH_2$ ), 0.40 (s, 3H, Si- $CH_3$ ), -0.04 (s, Si- $CH_3$ ). <sup>13</sup>C NMR (126 MHz,  $CD_2Cl_2$ ):  $\delta$  177.6 (d,  ${}^2J_{CP}$  = 2.9 Hz, N–C), 156.9 (d,  ${}^3J_{CP}$ = 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,  $C_{\text{Dipp}}$ ), 136.6 (br d,  $J_{\text{CF}}$  = 244.4 Hz,  $C_{\text{Ar}}$ -F), 134.3 (d,  $J_{\text{CP}}$  = 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,  $J_{CP} = 13.0 \text{ Hz}, \text{CH}_{Ph}$ ), 129.5 (s,  $CH_{dipp}$ ), 128.6 (d,  ${}^{1}J_{CP} = 91.3 \text{ Hz}, P-C_{Ph}$ ), 125.9 (s,  $CH_{dipp}$ ), 125.6 (s,  $CH_{dipp}$ ), 123.7 (d,  ${}^{1}J_{CP} = 89.6 \text{ Hz}, P-C_{Ph}$ ), 92.2 (d,  ${}^{1}J_{CP} = 73.2 \text{ Hz}, C-P$ ), 67.8 (d,  ${}^{2}J_{CP} = 10.6 \text{ Hz}, CH=C$ ), 56.0 (s,  $O-CH_3$ ), 52.1 (d,  ${}^{2}J_{CP} = 12.9 \text{ Hz}, CH_{bridgehead}$ ), 123.7 (L)  ${}^{2}J_{CP} = 12.9 \text{ Hz}, CH_{bridgehead}$ 49.9 (d,  ${}^{3}J_{CP}$  = 10.7 Hz, CH<sub>bridgehead</sub>), 46.9 (d,  $J_{CP}$  = 5.8 Hz, CH<sub>2</sub>), 28.8 (s,  $CH_{iPr}$ ), 28.5 (s,  $CH_2$ ), 28.4 (s,  $CH_{iPr}$ ), 28.3 (d,  ${}^{1}J_{CP}$  = 58.2 Hz, P- $CH_2$ ), 26.2 (d,  ${}^{3}J_{CP}$  = 2.8 Hz,  $CH_2$ ), 25.5 (s,  $CH_{3iPr}$ ), 25.1 (s,  $CH_{3iPr}$ ), 24.8 (s, CH<sub>3iPr</sub>), 23.7 (s, CH<sub>3iPr</sub>), -0.8 (s, Si-CH<sub>3</sub>), -1.6 (s, Si-CH<sub>3</sub>). C<sub>ipso</sub> attached to boron atom could not be detected. <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  20.9 (s). <sup>19</sup>F NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -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  $C_{Ar}$ - $F_{meta}$ ). <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -16.6 (s, BAr). <sup>29</sup>Si NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  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  $\mu$ L, 0.042 mmol). The reaction immediately proceeded to give adduct 7 as a mixture of two 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). Data for the major isomer (68%) are as follows. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.91–7.80 (m, 2H, CH<sub>Ph</sub>), 7.78–7.68 (m, 2H, CH<sub>Ph</sub>), 7.68–7.62 (m, 4H, CH<sub>Ph</sub>), 7.50–7.40 (m, 3H, CH<sub>Ph</sub>), 7.38–7.28 (m, 3H, CH<sub>Ph</sub>), 7.23–7.15 (m, 2H,

CH<sub>ph</sub>), 6.93-6.87 (m, 2H, CH<sub>ph</sub>), 6.39 (broad s, 1H, P-CH-O), 3.58 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H,  $CH_{iPr}$ ), 3.20 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H, 2  $CH_{iPr}$ ), 2.92 (br, 2H, 2  $CH_{bridgehead}$ ), 2.01–1.92 (m, 1H,  $CH_2$ ), 1.81–1.70 (m, 1H,  $CH_2$ ), 1.58–1.48 (m, 2H,  $CH_2$ ), 1.40 (d,  ${}^{3}J_{PH} = 6.9$  Hz, 3H, CH<sub>3iPr</sub>), 1.37–1.28 (m, 9H, 3 CH<sub>3iPr</sub>), 1.27–1.23 (m, 1H, CH<sub>2</sub>), 1.17-1.10 (m, 1H, CH<sub>2</sub>), 0.67 (s, 3H, Si-CH<sub>3</sub>), 0.02 (s, 3H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  177.9 (d, <sup>2</sup>J<sub>CP</sub> = 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<sub>Ph</sub>), 129.6 (s, CH<sub>Ph</sub>), 129.1 (d,  $J_{CP} = 2.6$  Hz, CH<sub>Ph</sub>), 127.9 (d,  $J_{CP} = 4.8$  Hz, CH<sub>Ph</sub>), 126.2 (s, 2 CH<sub>dipp</sub>), 125.8 (s, 2 CH<sub>dipp</sub>), 124.4 (br, B– C<sub>Ar</sub>), 118.7 (d,  $J_{CP} = 86.1$  Hz, P–C<sub>Ph</sub>), 116.3 (d,  $J_{CP} = 83.0$  Hz, P–  $C_{\text{Ph}}$ ), 90.0 (d,  ${}^{1}J_{\text{CP}}$  = 91.5 Hz, C–P), 73.4 (d,  ${}^{1}J_{\text{CP}}$  = 62.0 Hz, CH–O), 49.1 (d,  ${}^{2}J_{CP}$  = 10.9 Hz, CH<sub>bridgehead</sub>), 47.1 (d,  $J_{CP}$  = 5.7 Hz, CH<sub>2</sub>), 46.6 (d,  ${}^{2}J_{CP} = 8.4$  Hz, CH<sub>bridgehead</sub>), 28.7 (s, CH<sub>iPr</sub>), 28.6 (s, CH<sub>iPr</sub>), 27.9 (s, CH<sub>2</sub>), 26.6 (d,  ${}^{3}J_{CP} = 2.5$  Hz, CH<sub>2</sub>), 25.1 (s, CH<sub>3iPr</sub>), 24.9 (s, CH<sub>3iPr</sub>), 24.8 (s,  $CH_{3iPr}$ ), 24.5 (s,  $CH_{3iPr}$ ), 0.5 (s,  $Si-CH_3$ ), -1.4 (s,  $Si-CH_3$ ). <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 21.5 (s). <sup>19</sup>F NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -133.0 (br, C<sub>Ar</sub>-F<sub>ortho</sub>), -163.7 (t, J<sub>FF</sub> = 20.4 Hz, C<sub>Ar</sub>-F<sub>para</sub>), -167.5 (t, J<sub>FF</sub> = 18.1 Hz, C<sub>Ar</sub>-F<sub>meta</sub>). <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -16.6 (s, BAr). <sup>29</sup>Si NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.5 (s). Data for the minor isomer (32%) are as follows. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ):  $\delta$  7.91–7.80 (m, 1H,  $CH_{Ph}$ ), 7.78–7.68 (m, 1H,  $CH_{Ph}$ ), 7.68-7.62 (m, 4H, CH<sub>Ph</sub>), 7.51-7.40 (m, 3H, CH<sub>Ph</sub>), 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<sub>Ph</sub>), 6.39 (broad s, 1H, P-CH-O), 3.27 (sept,  ${}^{3}J_{HH} = 6.7$  Hz, 1H,  $CH_{iPr}$ ), 3.20 (m, 1H,  $CH_{iPr}$ ), 2.92 (br, 1H,  $CH_{\rm bridgehead}),~2.81$  (br, 1H,  $CH_{\rm bridgehead}),~2.01-1.92$  (m, 1H,  $CH_2),~1.92-1.82$  (m, 1H,  $CH_2),~1.79-1.70$  (m, 1H,  $CH_2),~1.58-1.48$  (m, 1H, CH<sub>2</sub>), 1.37–1.28 (m, 9H, 3 CH<sub>3*i*Pr</sub>), 1.21 (d,  ${}^{3}J_{PH} = 6.8$  Hz, 3H, CH<sub>3iPr</sub>), 1.17–1.10 (m, 1H, CH<sub>2</sub>), 1.03–0.96 (m, 1H, CH<sub>2</sub>), 0.85 (s, 3H, Si-CH<sub>3</sub>), 0.09 (s, 3H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  177.7 (d, <sup>2</sup> $J_{CP}$  = 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,  $C_{\text{Dipp}}$ ), 136.5 (br d,  $J_{\text{CF}}$  = 244.4 Hz,  $C_{\text{Ar}}$ -F), 135.7 (d,  $J_{\text{CP}}$  = 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  $(C_6H_5)_{benzaldehyde}$ ), 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 (d,  $J_{CP} = 4.2$  Hz,  $CH_{Ph}$ ), 125.8 (s,  $CH_{dipp}$ ), 125.7 (s,  $CH_{dipp}$ ), 124.4 (br, *ipso* of BAr), 119.7 (d, <sup>1</sup>J<sub>CP</sub> = 82.2 Hz, P- $C_{\rm Ph}$ ), 115.2 (d,  ${}^{1}J_{\rm CP}$  = 87.4 Hz, P- $C_{\rm Ph}$ ), 83.8 (d,  ${}^{1}J_{\rm CP}$  = 93.5 Hz, C-P), 73.5 (d,  $^{1}J_{CP} = 59.6$  Hz, P–CH–O), 49.8 (d,  $^{2}J_{CP} = 10.5$  Hz, CH<sub>bridgehead</sub>), 48.0 (d,  $^{2}J_{CP} = 10.4$  Hz, CH<sub>bridgehead</sub>), 46.0 (d,  $^{J}_{CP} = 4.0$  Hz, CH<sub>2</sub>), 28.7 (s, CH<sub>iPr</sub>), 28.5 (s, CH<sub>iPr</sub>), 28.3 (s, CH<sub>2</sub>), 26.4 (d,  ${}^{3}J_{CP}$  = 2.5 Hz, CH<sub>2</sub>), 25.4 (s, CH<sub>3iPr</sub>), 25.0 (s, CH<sub>3iPr</sub>), 24.7 (s, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -133.0 (br, C<sub>Ar</sub>-F<sub>ortho</sub>), -163.7 (t, J<sub>FF</sub> = 20.4 Hz, C<sub>Ar</sub>-F<sub>para</sub>), -167.5 (t, J<sub>FF</sub> = 18.1 Hz, C<sub>Ar</sub>-F<sub>meta</sub>). <sup>11</sup>B NMR (160 MHz,  $CD_2Cl_2$ ):  $\delta - 16.6$  (s, BAr). <sup>29</sup>Si NMR (99 MHz,  $CD_2Cl_2$ ):  $\delta 8.9$  (s).

#### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00489.

Spectroscopic and X-ray data (PDF)

#### Accession Codes

CCDC 2016527–2016532 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# **Author Contributions**

A.D. performed all synthetic work, while N.S.-M. performed all X-ray structural studies.

#### Notes

The authors declare no competing financial interest.

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