

# Anionic 1,4-Silyl Migration in (2-(Trimethylsilyl)phenyl)phosphonium Methylides

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**Summary:** To investigate the intramolecular 1,5-type C<sup>−</sup>⋯Si interaction, (2-(trimethylsilyl)phenyl)phosphonium methylides **1** were prepared. Treatment of the precursors, the methyl(2-(trimethylsilyl)phenyl)phosphonium iodides **2** (R = Ph, Me), with sodium hexamethyldisilazide in THF afforded the phosphonium methylides **1**, which readily underwent anionic 1,4-silyl migration to form the silylated ylides **4** at low temperatures. They were characterized by NMR and trapping experiments.

## Introduction

The intramolecular 1,5-type interaction between an electron-donating heteroatom (Y) and a tetracoordinate silicon, which are linked to each other through the *o*-phenylene skeleton (Figure 1), has been widely studied, because this type of interaction sometimes realizes the hypercoordination at the silicon.<sup>1</sup> A number of coordinating groups (−X−Y) are available, such as −CH<sub>2</sub>−Y (Y = NR<sub>2</sub>, OR, PR<sub>2</sub>, SR),<sup>1,2</sup> −CF<sub>2</sub>−F,<sup>1</sup> −NR′−NR<sub>2</sub>,<sup>1</sup> −N=NR,<sup>3</sup> and −P(OR)<sub>2</sub>=O.<sup>4</sup>

In contrast, the intramolecular 1,5-type interaction between a carbanion moiety (Y = CR<sub>2</sub><sup>−</sup>) and a tetracoordinate silicon has been little explored. Vedejs et al. previously reported that  $\alpha$ -lithiophosphate (X = P(=O)(OEt), Y = CH<sub>2</sub>Li) underwent an 1,4-silyl migration.<sup>5,6</sup> To obtain insight into such an interaction, we chose phosphonium ylides as the coordinating groups<sup>7</sup> and have attempted to prepare compounds in which the phosphonium ylide site (X = PR<sub>2</sub><sup>+</sup>, Y = CH<sub>2</sub><sup>−</sup>) is linked through the *o*-phenylene skeleton to the tetracoordinate silicon,

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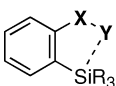
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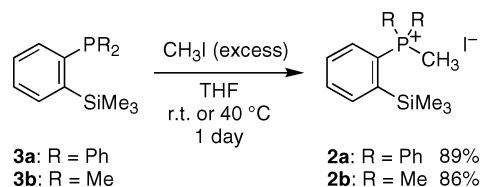
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X	Y
−CH <sub>2</sub> −	NR <sub>2</sub> , OR, PR <sub>2</sub> , SR
−CF <sub>2</sub> −	F
−NR′−	NR <sub>2</sub>
−N=	NR
−P(OR′) <sub>2</sub> =	O

**Figure 1.** Representative coordinating groups in 1,5-type interactions in hypercoordinate silicon compounds.

## Scheme 1



thereby allowing for the 1,5-type C<sup>−</sup>⋯Si interaction. In the course of our study of such compounds, we have discovered a 1,4-silyl migration in (2-(trimethylsilyl)phenyl)phosphonium methylides **1**.

## Results and Discussion

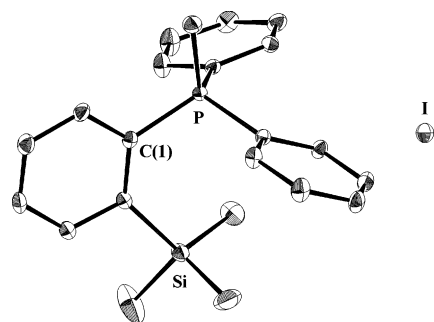
Methyl(2-(trimethylsilyl)phenyl)phosphonium iodides **2**, the precursors of **1**, were prepared from the corresponding phosphines **3** and methyl iodide in THF, as shown in Scheme 1.<sup>8,9</sup> The structures of **2** were confirmed by X-ray crystallographic analysis, as shown in Figures 2 and 3. We may notice that the methyl group in **2a** (Figure 2), which will be deprotonated by a base, faces away from the silyl group to be coordinated.

We expected that the treatment of **2** with a base would give phosphonium ylides **1**, in which the ylidic carbon would intramolecularly coordinate to the silicon. Treatment of **2a** with sodium hexamethyldisilazide<sup>10</sup> (NaHMDS) in THF at 0 °C, however, afforded the silylated ylide **4a**, as shown in Scheme 2. The NMR spectra of the reaction mixture showed the <sup>1</sup>H resonance at  $\delta$  −0.15 (d, <sup>2</sup>J<sub>H−P</sub> = 9 Hz, 1H, for CH), the <sup>29</sup>Si resonance at  $\delta$  −8.9 (d, <sup>2</sup>J<sub>Si−P</sub> = 17 Hz), and the <sup>31</sup>P resonance

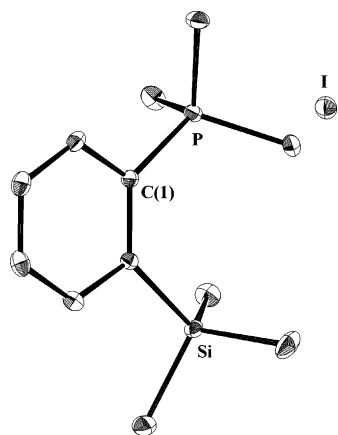
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(9) Crystallographic data for **2a** and **2b** have been deposited with the Cambridge Crystallographic Data Center as Nos. CCDC-281807 (**2a**) and CCDC-281808 (**2b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336-033; e-mail, deposit@ccdc.cam.ac.uk). See also the Supporting Information.

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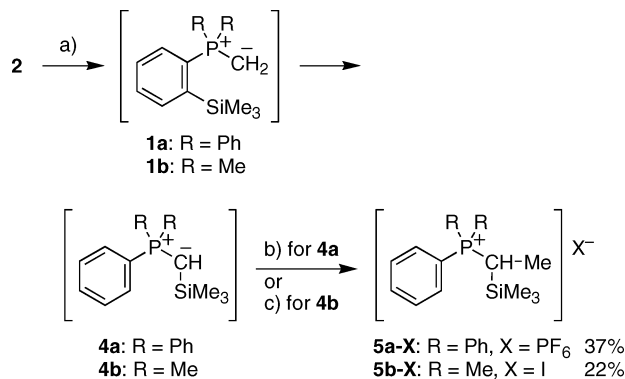


**Figure 2.** Molecular structure of **2a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.



**Figure 3.** Molecular structure of **2b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

### Scheme 2<sup>a</sup>



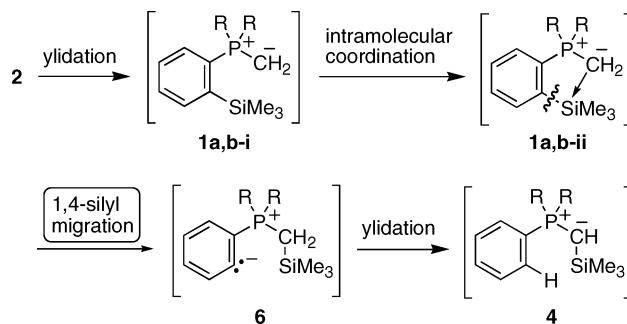
<sup>a</sup> Legend: (a) NaHMDS ( $\times 1$ )/THF/0 °C, 1–2.5 h; (b) (i) MeI ( $\times 5$ )/Et<sub>2</sub>O/room temperature, 2.5 h, (ii) KPF<sub>6</sub> ( $\times 1.5$ )/CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O/room temperature, 2 h; (c) MeI ( $\times 10$ )/THF/0 °C, 1 h and room temperature, 0.5 h.

at  $\delta$  21.9. Treatment of **2b** with NaHMDS under similar reaction conditions afforded **4b**. The NMR spectra showed the <sup>1</sup>H resonances at  $\delta$  –0.70 (d, <sup>2</sup>J<sub>H–P</sub> = 9 Hz, 1H for CH) and  $\delta$  +1.58 (d, <sup>2</sup>J<sub>H–P</sub> = 13 Hz, 6H for PMe<sub>2</sub>), the <sup>29</sup>Si resonance at  $\delta$  –10.0 (d, <sup>2</sup>J<sub>Si–P</sub> = 16 Hz), and the <sup>31</sup>P resonance at  $\delta$  6.9. The observed spectra were consistent with those of **4a** and **4b** prepared by conventional procedures.<sup>11</sup>

The formation of **4** was also confirmed by trapping experiments, as shown in Scheme 2.<sup>12</sup> The phosphonium ylide **4a** was allowed to react with MeI,<sup>13</sup> giving the phosphonium iodide **5a-I**. Since the poor crystallinity of **5a-I** made its purification

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### Scheme 3



difficult, it was converted into the phosphonium hexafluorophosphate **5a-PF<sub>6</sub>** in an overall 37% yield by use of KPF<sub>6</sub>.<sup>14</sup> The phosphonium ylide **4b** was reacted with MeI<sup>13</sup> to give the phosphonium iodide **5b-I** in 22% yield as colorless crystals.

To monitor the reaction, **2a** was exposed to NaHMDS in THF-*d*<sub>8</sub> at –78 °C and subjected to variable-temperature NMR experiments (see the Supporting Information). At –78 °C the <sup>1</sup>H resonance was found at  $\delta$  0.18 (d, <sup>2</sup>J<sub>P–H</sub> = 8 Hz, 2H for CH<sub>2</sub>), the <sup>29</sup>Si resonance at  $\delta$  –4.2 (d, <sup>3</sup>J<sub>Si–P</sub> = 4.9 Hz), and the <sup>31</sup>P resonance at  $\delta$  26.0, which were different from those of **4a** but were assignable to **1a**. When the temperature was raised to –20 °C, the peaks of **4a** appeared in addition to those of **1a**. At room temperature, the peaks of **1a** disappeared and only those of **4a** were observed. In contrast to this, when **2b** was used, only **4b** was observed at –78 °C. Thus, the silyl migration in **1b** proceeds even at –78 °C and is much faster than that in **1a**.

One plausible mechanism of formation of **4** is as follows (Scheme 3). The <sup>29</sup>Si shift in **1a** ( $\delta$  –4.2) can be attributed to the tetracoordinate species **1a-i**, since the <sup>29</sup>Si resonances of the pentaorganosilicates<sup>15</sup> were reported to be in the range between  $\delta$  –110 and –130. At low temperature the two bulky phenyl groups on the phosphorus in **1a** may retard the coordination of the ylidic carbon to the silicon. On the other hand, the ylidic carbon in **1b** is more readily accessible to the silicon, owing to the less sterically demanding methyl groups. Thus, the pentacoordinate state should be achieved at elevated temperatures in **1a** but even at –78 °C in **1b**. Once pentacoordinate **1a-ii** and **1b-ii** are formed, both of them readily undergo the silyl migration through activation of the endocyclic Si–C(sp<sup>2</sup>) bond.

The resulting zwitterion **6** may be so unstable that the phenyl anion portion immediately abstracts a methylene proton between the phosphorus and the silicon, resulting in the formation of silylated ylide **4**. The driving force of the migration may be attributed to the thermodynamic stability of silicon-stabilized ylide **4** compared to that of the nonstabilized ylide **1**. It is also noted that the intramolecularity of the silyl migration was confirmed by the fact that the reaction between **3a** and

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triphenylphosphonium methylide<sup>11a</sup> did not produce the silylated ylide **4a** at all.

It remains debatable whether the pentaorganosilicate **1a-ii** is an intermediate or a transition state, because Schmidbaur et al.<sup>16</sup> mentioned the corresponding species as a transition state in the 1,3-silyl migration in the ((trimethylsilyl)methyl)phosphonium ylides, whereas Vedejs et al.<sup>5</sup> described the pentaorganosilicate as an intermediate in the 1,4-silyl migration in the  $\alpha$ -lithio-phosphinate.

In conclusion, the intramolecular 1,5-type C<sup>-</sup>...Si interactions in (2-(trimethylsilyl)phenyl)phosphonium methylides **1** were investigated. The plausible pentacoordinate silicates are so transient that they readily undergo the 1,4-silyl migration to afford silylated ylides **4**. The present case indicates that the ylidic carbon of the phosphonium methylides has sufficient coordinating ability to the silicon.<sup>5</sup> It is also found that the rate of the migration depends on the substituents on the phosphorus. Our current effort is focused on the stabilization of the pentacoordinate silicates by steric or electronic tuning of the substituents at the phosphorus and/or the silicon.

## Experimental Section

**General Considerations.** The <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), <sup>19</sup>F (376 MHz), <sup>29</sup>Si (80 MHz), and <sup>31</sup>P (162 MHz) NMR spectra were recorded using a JEOL EX-400 or AL-400 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to the internal CDCl<sub>3</sub> (<sup>1</sup>H,  $\delta$  7.26 ppm; <sup>13</sup>C,  $\delta$  77.00 ppm) and THF-*d*<sub>8</sub> (<sup>1</sup>H,  $\delta$  3.58 ppm; <sup>13</sup>C,  $\delta$  67.4 ppm). <sup>19</sup>F chemical shifts were referenced to external CFCl<sub>3</sub> ( $\delta$  0 ppm). <sup>29</sup>Si chemical shifts were referenced to external tetramethylsilane ( $\delta$  0 ppm). <sup>31</sup>P chemical shifts were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0 ppm). The mass spectra were measured at 70 eV using a JEOL SX-102A mass spectrometer. The elemental analyses were performed using the Perkin-Elmer 2400CHN elemental analyzer at our laboratory or using the Perkin-Elmer CHNS/O 2400II elemental analyzer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. The analytical samples were purified by recrystallization. Melting points were measured with a Yanaco Micro melting point apparatus and were uncorrected.

Trimethylphenylphosphonium iodide was prepared by reaction of dimethylphenylphosphine and methyl iodide. Chlorotrimethylsilane was treated with small pieces of sodium under a nitrogen atmosphere to remove dissolved HCl, and the supernatant was used. Methyl iodide (MeI) was dried over molecular sieves 4A prior to use. Sodium hexamethyldisilazide (NaHMDS) in THF was purchased from the Aldrich Co. or Kanto Chemical Co., Inc. Butyllithium (*n*-BuLi) in hexane and potassium hexafluorophosphate (KPF<sub>6</sub>) were purchased from Kanto Chemical Co., Inc. Hexane was distilled under a nitrogen atmosphere over calcium hydride. THF, THF-*d*<sub>8</sub>, and Et<sub>2</sub>O were distilled under a nitrogen atmosphere over sodium diphenylketyl. All reactions were carried out under an inert gas atmosphere.

**(2-Bromophenyl)diphenylphosphine.** This compound was prepared according to the procedures reported in the literature.<sup>8a</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 6.63–6.66 (m, 1H), 7.06–7.11 (m, 2H), 7.15–7.20 (m, 4H), 7.22–7.29 (m, 4H), 7.36–7.41 (m, 1H), 7.45–7.50 (m, 1H), 7.57–7.64 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 127.2, 128.7 (d, <sup>3</sup>J<sub>C-P</sub> = 8 Hz), 128.9, 129.8 (d, <sup>2</sup>J<sub>C-P</sub> = 31 Hz), 130.0, 132.8 (d, <sup>2</sup>J<sub>C-P</sub> = 3 Hz), 133.8 (d, <sup>2</sup>J<sub>C-P</sub> = 21 Hz), 134.3 (d, <sup>2</sup>J<sub>C-P</sub> = 2 Hz), 135.6 (d, <sup>1</sup>J<sub>C-P</sub> = 10 Hz), 138.7 (d, <sup>1</sup>J<sub>C-P</sub> = 12 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): -4.5.

**(2-Bromophenyl)dimethylphosphine.** This compound was prepared according to the procedures reported in the literature.<sup>8</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.37 (d, <sup>2</sup>J<sub>H-P</sub> = 4 Hz, 6H), 7.15–7.19 (m, 1H),

7.33–7.35 (m, 2H), 7.54–7.57 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 13.6 (d, <sup>1</sup>J<sub>C-P</sub> = 13 Hz), 127.3, 129.2 (d, <sup>2</sup>J<sub>C-P</sub> = 19 Hz), 129.4, 129.9, 132.7 (d, <sup>2</sup>J<sub>C-P</sub> = 3 Hz), 142.3 (d, <sup>1</sup>J<sub>C-P</sub> = 16 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): -41.8.

**Preparation of Diphenyl(2-(trimethylsilyl)phenyl)phosphine (3a).** A solution of *n*-BuLi in hexane (1.6 M, 6.30 mL, 10.1 mmol) was added over 5 min to a solution of (2-bromophenyl)diphenylphosphine (3.41 g, 9.99 mmol) in Et<sub>2</sub>O (30 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 50 min. Then chlorotrimethylsilane (1.40 mL, 11.1 mmol) was added over 3 min to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for a further 3 h. A saturated aqueous solution of NH<sub>4</sub>Cl (30 mL) was added to the reaction mixture. The mixture was extracted with Et<sub>2</sub>O (30 mL  $\times$  3), and the combined organic layers were dried over Mg<sub>2</sub>SO<sub>4</sub>. The solution was concentrated in vacuo, and the residue (3.36 g) was subjected to column chromatography on silica gel (150 mL) with hexane as eluent (*R*<sub>f</sub> = 0.40) to give **3a** (2.74 g, 82% yield) as a white solid. Mp: 50.5–52.7 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.38 (d, <sup>5</sup>J<sub>H-P</sub> = 1.2 Hz, 9H), 7.15–7.18 (m, 1H), 7.20–7.25 (m, 4H), 7.29–7.36 (m, 8H), 7.62–7.65 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.6 (d, <sup>4</sup>J<sub>C-P</sub> = 9 Hz), 128.0, 128.16, 128.23, 129.0, 133.1 (d, <sup>2</sup>J<sub>C-P</sub> = 18 Hz), 134.5 (d, <sup>2</sup>J<sub>C-P</sub> = 17 Hz), 135.2 (d, <sup>3</sup>J<sub>C-P</sub> = 2 Hz), 138.2 (d, <sup>1</sup>J<sub>C-P</sub> = 12 Hz), 142.9 (d, <sup>1</sup>J<sub>C-P</sub> = 12 Hz), 148.0 (d, <sup>2</sup>J<sub>C-P</sub> = 47 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>,  $\delta$ ): -3.5 (d, <sup>3</sup>J<sub>Si-P</sub> = 10 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): -9.6. MS (EI): *m/z* 334 (M<sup>+</sup>, 33), 319 (M<sup>+</sup> - Me, 100). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>SiP: C, 75.41; H, 6.93. Found: C, 75.56; H, 7.02.

**Preparation of Dimethyl(2-(trimethylsilyl)phenyl)phosphine (3b).** A solution of *n*-BuLi in hexane (1.58 M, 9.00 mL, 14.2 mmol) was added over 5 min to a solution of (2-bromophenyl)dimethylphosphine (3.08 g, 14.2 mmol) in Et<sub>2</sub>O (28 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 4 h. Then chlorotrimethylsilane (2.70 mL, 21.3 mmol) was added over 5 min to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for a further 2 h. The reaction mixture was diluted with hexane (30 mL) and filtered through a glass fiber pad. The filtrate was concentrated in vacuo, and the residue was distilled under reduced pressure (43–56 °C/0.2 mmHg) to give **3b** (1.88 g, 63% yield) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.40 (d, <sup>5</sup>J<sub>H-P</sub> = 1.6 Hz, 9H), 1.26 (d, <sup>2</sup>J<sub>H-P</sub> = 4 Hz, 6H), 7.30–7.34 (m, 1H), 7.38–7.42 (m, 1H), 7.52–7.55 (m, 1H), 7.64–7.66 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.6 (d, <sup>4</sup>J<sub>C-P</sub> = 11 Hz), 15.5 (d, <sup>1</sup>J<sub>C-P</sub> = 13 Hz), 127.9 (d, <sup>3</sup>J<sub>C-P</sub> = 2 Hz), 129.0, 129.5 (d, <sup>3</sup>J<sub>C-P</sub> = 3 Hz), 134.0 (d, <sup>2</sup>J<sub>C-P</sub> = 16 Hz), 146.5 (d, <sup>2</sup>J<sub>C-P</sub> = 47 Hz), 147.8 (d, <sup>1</sup>J<sub>C-P</sub> = 13 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>,  $\delta$ ): -3.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): -53.8. MS (EI): *m/z* 211 (M<sup>+</sup> + 1, 100), 210 (M<sup>+</sup>, 6), 195 (M<sup>+</sup> - Me, 40). Anal. Calcd for C<sub>11</sub>H<sub>19</sub>SiP: C, 62.82; H, 9.11. Found: C, 63.19; H, 9.06.

**Preparation of Methyl(diphenyl(2-(trimethylsilyl)phenyl)phosphonium Iodide (2a).** Methyl iodide (0.85 mL, 13.6 mmol) was added to a solution of **3a** (1.27 g, 3.80 mmol) in THF (5.0 mL) at room temperature, and the reaction mixture was heated at 40 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered. The obtained precipitate was dried in vacuo and recrystallized from EtOH–hexane to afford **2a** (1.61 g, 89% yield) as colorless crystals. Mp: 189.0–190.1 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.10 (s, 9H), 3.27 (d, <sup>2</sup>J<sub>H-P</sub> = 13 Hz, 3H), 7.29–7.35 (m, 1H), 7.52–7.55 (m, 1H), 7.68–7.82 (m, 11H), 8.01–8.04 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 2.0, 13.4 (d, <sup>1</sup>J<sub>C-P</sub> = 56 Hz), 120.0 (d, <sup>1</sup>J<sub>C-P</sub> = 88 Hz), 122.6 (d, <sup>1</sup>J<sub>C-P</sub> = 87 Hz), 129.6 (d, <sup>3</sup>J<sub>C-P</sub> = 13 Hz), 130.2 (d, <sup>3</sup>J<sub>C-P</sub> = 13 Hz), 133.0 (d, <sup>3</sup>J<sub>C-P</sub> = 11 Hz), 133.4 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz), 134.8 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz), 136.2 (d, <sup>2</sup>J<sub>C-P</sub> = 15 Hz), 138.7 (d, <sup>2</sup>J<sub>C-P</sub> = 17 Hz), 146.5 (d, <sup>2</sup>J<sub>C-P</sub> = 19 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>,  $\delta$ ): -0.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): 25.0. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>SiPI: C, 55.46; H, 5.50. Found: C, 55.34; H, 5.72.



**Preparation of Trimethyl(2-(trimethylsilyl)phenyl)phosphonium Iodide (2b).** Methyl iodide (0.48 mL, 7.71 mmol) was added to a solution of **3b** (539 mg, 2.56 mmol) in THF (7.5 mL) at room temperature, and the reaction mixture was stirred at room temperature for 22 h. Then the reaction mixture was filtered. The obtained precipitate was dried in vacuo and recrystallized from EtOH to afford **2b** (778 mg, 86% yield) as colorless crystals. Mp: 232.0–233.7 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.51 (s, 9H), 2.65 (d, <sup>2</sup>J<sub>H-P</sub> = 14 Hz, 9H), 7.62–7.67 (m, 1H), 7.68–7.73 (m, 1H), 7.79–7.84 (m, 1H), 7.92–7.95 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 2.7, 13.3 (d, <sup>1</sup>J<sub>C-P</sub> = 54 Hz), 126.7 (d, <sup>1</sup>J<sub>C-P</sub> = 83 Hz), 130.1 (d, <sup>3</sup>J<sub>C-P</sub> = 13 Hz), 133.1 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.4 (d, <sup>3</sup>J<sub>C-P</sub> = 14 Hz), 138.1 (d, <sup>2</sup>J<sub>C-P</sub> = 16 Hz), 144.1 (d, <sup>2</sup>J<sub>C-P</sub> = 19 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): -1.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>, δ): 23.3. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>SiPI: C, 40.91; H, 6.29. Found: C, 40.80; H, 6.42.

**Generation of Triphenylphosphonium (Trimethylsilyl)methylide (4a).** To a suspension of **2a** (47 mg, 0.099 mmol) in THF-*d*<sub>8</sub> (1.0 mL) was added NaHMDS in THF (1.0 M, 0.10 mL, 0.10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, giving a clear yellow solution of **4a**. The reaction solution (ca. 0.6 mL) was transferred to a Young valve NMR tube under an inert gas atmosphere and subjected to the NMR measurements. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, δ): -0.27 (s, 9H), -0.15 (d, <sup>2</sup>J<sub>H-P</sub> = 9 Hz, 1H), 7.35–7.44 (m, 9H), 7.59–7.64 (m, 6H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, δ): -1.3 (d, <sup>1</sup>J<sub>C-P</sub> = 96 Hz), 4.2 (d, <sup>3</sup>J<sub>C-P</sub> = 4 Hz), 128.8 (d, <sup>3</sup>J<sub>C-P</sub> = 11 Hz), 131.4 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.4 (d, <sup>2</sup>J<sub>C-P</sub> = 10 Hz), 135.2 (d, <sup>1</sup>J<sub>C-P</sub> = 84 Hz). <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, δ): -8.9 (d, <sup>2</sup>J<sub>Si-P</sub> = 17 Hz). <sup>31</sup>P NMR (THF-*d*<sub>8</sub>, δ): 21.9.

**Generation of Dimethylphenylphosphonium (Trimethylsilyl)methylide (4b).** To a suspension of **2b** (36 mg, 0.10 mmol) in THF-*d*<sub>8</sub> (1.0 mL) was added NaHMDS in THF (1.0 M, 0.10 mL, 0.10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, giving a clear yellow solution of **4b**. The reaction solution (ca. 0.6 mL) was transferred to a Young valve NMR tube under an inert gas atmosphere and subjected to the NMR measurements. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, δ): -0.70 (d, <sup>2</sup>J<sub>H-P</sub> = 9 Hz, 1H), -0.09 (s, 9H), 1.58 (d, <sup>2</sup>J<sub>H-P</sub> = 13 Hz, 6H), 7.35–7.37 (m, 3H), 7.78–7.83 (m, 2H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, δ): -2.0 (d, <sup>1</sup>J<sub>C-P</sub> = 93 Hz), 4.8 (d, <sup>3</sup>J<sub>C-P</sub> = 4 Hz), 18.8 (s, <sup>1</sup>J<sub>C-P</sub> = 61 Hz), 128.6 (d, <sup>3</sup>J<sub>C-P</sub> = 11 Hz), 130.7 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz), 131.1 (d, <sup>2</sup>J<sub>C-P</sub> = 11 Hz), 139.4 (d, <sup>1</sup>J<sub>C-P</sub> = 74 Hz). <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, δ): -10.0 (d, <sup>2</sup>J<sub>Si-P</sub> = 16 Hz). <sup>31</sup>P NMR (THF-*d*<sub>8</sub>, δ): 6.9.

**Trapping Experiment of 4a with MeI and Counteranion Exchange: Formation of Triphenyl(1-(trimethylsilyl)ethyl)phosphonium Hexafluorophosphate (5a).** To a suspension of **2a** (238 mg, 0.50 mmol) in THF (5.0 mL) was added NaHMDS in THF (1.1 M, 0.46 mL, 0.51 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, giving a clear yellow solution of **4a**. The solvents were removed under reduced pressure, and the residue was dissolved in Et<sub>2</sub>O (4.0 mL). The solution of **4a** in Et<sub>2</sub>O was added over 80 min to a solution of MeI (0.16 mL, 2.5 mmol) in Et<sub>2</sub>O (1.0 mL) at room temperature. The reaction mixture was stirred for a further 75 min at room temperature, giving a colorless solution. The solvents were removed under reduced pressure, and the residue was dissolved in dichloromethane (2.0 mL). To this solution was added a solution of KPF<sub>6</sub> (140 mg, 0.76 mmol) in water (2.0 mL), and the reaction mixture was vigorously stirred at room temperature for 2 h. Then the mixture was extracted with dichloromethane (2 mL × 3) and the combined organic layers were dried over MgSO<sub>4</sub>. The solution was concentrated in vacuo. The obtained solid was recrystallized from dichloromethane–Et<sub>2</sub>O to afford **5a** (95 mg, 37% yield) as colorless crystals. Mp: 185.6–187.1 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): -0.10 (s, 9H), 1.46 (dd, <sup>3</sup>J<sub>H-P</sub> = 20 Hz, *J* = 7

Hz, 3H), 3.31 (dq, <sup>2</sup>J<sub>H-P</sub> = 18 Hz, *J* = 7 Hz, 1H), 7.66–7.85 (m, 15H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): -1.2 (d, <sup>3</sup>J<sub>C-P</sub> = 3 Hz), 10.0 (d, <sup>2</sup>J<sub>C-P</sub> = 5 Hz), 10.9 (d, <sup>1</sup>J<sub>C-P</sub> = 39 Hz), 119.3 (d, <sup>1</sup>J<sub>C-P</sub> = 84 Hz), 130.3 (d, <sup>3</sup>J<sub>C-P</sub> = 12 Hz), 133.1 (d, <sup>2</sup>J<sub>C-P</sub> = 9 Hz), 134.6 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, δ): -73.2 (d, <sup>1</sup>J<sub>F-P</sub> = 720 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): 7.9. <sup>31</sup>P NMR (CDCl<sub>3</sub>, δ): -143.6 (quint, <sup>1</sup>J<sub>P-F</sub> = 720 Hz), 30.3. Anal. Calcd for C<sub>23</sub>H<sub>28</sub>F<sub>6</sub>SiP<sub>2</sub>: C, 54.33; H, 5.55. Found: C, 54.42; H, 5.53.

**Trapping Experiment of 4b with MeI: Formation of Dimethylphenyl(1-(trimethylsilyl)ethyl)phosphonium Iodide (5b).** To a suspension of **2b** (176 mg, 0.50 mmol) in THF (5.0 mL) was added NaHMDS in THF (1.1 M, 0.46 mL, 0.51 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2.5 h, giving a clear yellow solution of **4b**. The solution was added to a solution of MeI (0.31 mL, 5.0 mmol) in THF (2.0 mL) at 0 °C over 5 min. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 0.5 h. Then the solvents were removed under reduced pressure and the residue was dissolved in chloroform (7 mL). The resulting precipitate was filtered off. The filtrate was concentrated in vacuo. The residue was crystallized from ethanol–hexane and then ethanol–Et<sub>2</sub>O to afford **5b** (40 mg, 22% yield) as colorless crystals. Mp: 144.5–146.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.09 (s, 9H), 1.38 (dd, <sup>3</sup>J<sub>H-P</sub> = 21 Hz and <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 3H), 2.42 (d, <sup>2</sup>J<sub>H-P</sub> = 13 Hz, 3H), 2.45 (d, <sup>2</sup>J<sub>H-P</sub> = 13 Hz, 3H), 2.90 (dq, <sup>2</sup>J<sub>H-P</sub> = 21 Hz and <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 1H), 7.65–7.76 (m, 3H), 7.93–7.98 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): -0.9 (d, <sup>3</sup>J<sub>C-P</sub> = 2 Hz), 9.76 (d, <sup>2</sup>J<sub>C-P</sub> = 4 Hz), 9.78 (d, <sup>1</sup>J<sub>C-P</sub> = 55 Hz), 9.88 (d, <sup>1</sup>J<sub>C-P</sub> = 55 Hz), 14.9 (d, <sup>1</sup>J<sub>C-P</sub> = 40 Hz), 121.4 (d, <sup>1</sup>J<sub>C-P</sub> = 83 Hz), 129.8 (d, <sup>3</sup>J<sub>C-P</sub> = 12 Hz), 131.4 (d, <sup>2</sup>J<sub>C-P</sub> = 10 Hz), 134.1 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): 6.4 (d, <sup>2</sup>J<sub>Si-P</sub> = 2 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>, δ): 29.6. Anal. Calcd for: C, 42.63; H, 6.60. Found: C, 42.69; H, 6.36.

**Synthesis of 4a by a Conventional Procedure.**<sup>11b</sup> To a solution of triphenylphosphonium methylide<sup>11a</sup> (2.46 g, 8.90 mmol) in THF (50 mL) was added chlorotrimethylsilane (0.56 mL, 4.4 mmol) in THF (10 mL) at room temperature. The reaction mixture was refluxed for 5 h. After the solution was concentrated, the residue was diluted with hexane (40 mL) and this solution was filtered. The filtrate was concentrated to give **4a** (1.33 g, 43% yield) as a yellow solid. The obtained **4a** was directly subjected to the NMR measurements.

**Synthesis of 4b by a Conventional Procedure.**<sup>11b</sup> To a suspension of trimethylphenylphosphonium iodide (279 mg, 1.00 mmol) in THF (10 mL) was added a solution of NaHMDS in THF (1.1 M, 0.90 mL, 0.99 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h. A solution of chlorotrimethylsilane (0.065 mL, 0.51 mmol) in THF (4.0 mL) was added over 3 min to the reaction mixture. After being stirred at room temperature for 18 h, the solution was concentrated, the residue was diluted with Et<sub>2</sub>O (10 mL), and this solution was filtered. The filtrate was concentrated in vacuo to afford **4b** (26 mg, 11% yield) as a yellow oil. The obtained **4b** was directly subjected to the NMR measurements.

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**Supporting Information Available:** Figures and tables giving variable-temperature NMR spectra of **1a/4a** and **4b** and X-ray crystallographic data of **2a** and **2b**; these X-ray data are also given as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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