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Synthesis of Functional Phosphines with Ortho-Substituted Aryl Groups: 2-$RC_6H_4PH_2$ and 2-$RC_6H_4P(SiMe_3)_2$ (R = 2-*i*-Pr- or 2-*t*-Bu-)

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ABSTRACT: *The synthesis and characterization of 2-*i*-$PrC_6H_4PCl_2$ (**3**), 2-*t*-$BuC_6H_4PCl_2$ (**4**), 2-*i*-$PrC_6H_4PH_2$ (**5**), 2-*t*-$BuC_6H_4PH_2$ (**6**), 2-*i*-$PrC_6H_4P(SiMe_3)_2$ (**7**), and 2-*t*-$BuC_6H_4P(SiMe_3)_2$ (**8**) are described.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:265–270, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20606

INTRODUCTION

The development of chemically functional phosphines bearing sterically encumbering substituents has had a profound impact on the low-coordinate chemistry of phosphorus. For example, the employment *P*-substituents such as 2,4,6-$Me_3C_6H_2$— (mesityl, Mes) and 2,4,6-*t*-$Bu_3C_6H_2$— (supermesityl, Mes*) permitted the isolation of the phosphaalkene $MesP{=}CPh_2$ [1] and the diphosphene Mes*P=PMes* [2]. Recently, the development of bulkier and more sophisticated aryl substituents [e.g., 2,6-{2,4,6-(*i*-$Pr)_3C_6H_2\}_2C_6H_3$— and 2,4,6-$\{CH(SiMe_3)_2\}_3C_6H_2$—] led to the isolable compounds of the heavier elements of the periodic table with low-coordination numbers [3].

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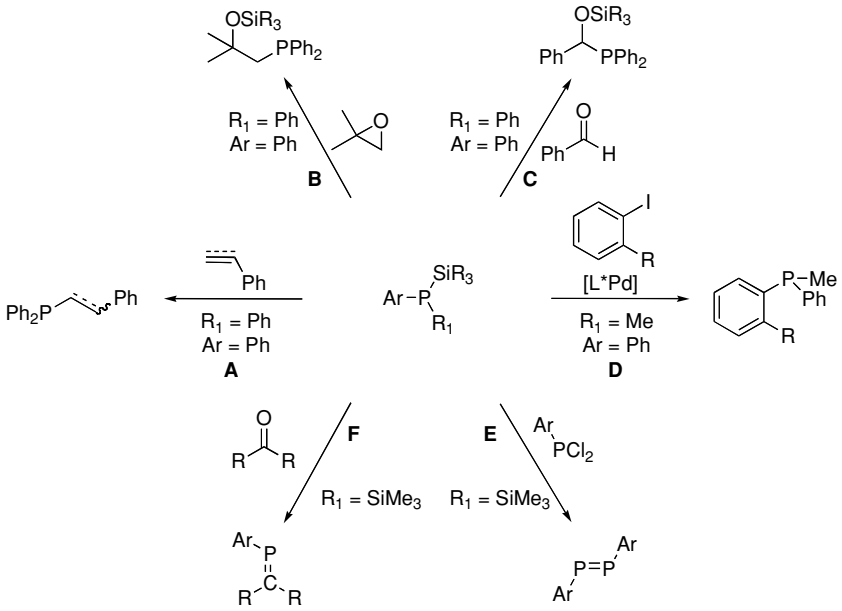
Combining a P-aryl substituent with P-H or P-$SiMe_3$ functional groups at phosphorus results in reactive phosphines that are important building blocks in organic, main group, and organometallic chemistry [4,5]. Several representative reactions are shown in Scheme 1 to illustrate the utility of phosphines with P-Si functionalities. Phosphines with a single trimethylsilyl substituent may be employed to functionalize alkenes and alkynes **A** [6–12], ring-open epoxides **B** [13], add to aldehydes **C** [13–15], and support metal-catalyzed coupling reactions **D** [16–18]. In addition, bis(trimethylsilyl)phosphines are important precursors to diphosphenes **E** [19], and phosphaalkenes **F** [20] when appropriately bulky aryl substituents (Ar) are employed.

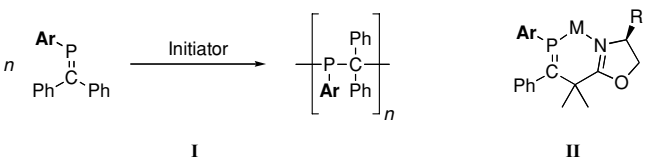
We [21], and others [22], are interested in the development of applications for phosphaalkenes in areas such as polymer science and catalysis (Scheme 2, **I** and **II**). We have demonstrated that a delicate balance between kinetic and thermodynamic stability is required to afford isolable but polymerizable monomers. For example, mesityl-substituted $MesP{=}CPh_2$ polymerizes [23], whereas we have been unsuccessful in polymerizing supermesityl-substituted Mes*P=CH_2 [24]. The polymerization of P=C bonds opens the door to the generation of a wide range of functional homopolymers, or block- or random-copolymers, that are effective in binding transition metals [25,26], forming self-assembled nanostructures, and as ligands for use



SCHEME 1

in polymer-supported catalysts [27]. In addition, we have recently been interested in the development of phosphaalkene-based ligands for use in asymmetric catalysis (Scheme 2, **II**) [28,29].

To tune the steric properties of phosphaalkenes for application in catalysis and polymer science, we have been interested in the development of moderately bulky P-aryl substituents with a single substituent in the ortho-position. Since (2-MeC_6H_4)P=CPh_2 was reported to be unstable [1], we pursued the preparation of systems with the slightly larger *i*-Pr or *t*-Bu substituent in the 2-position of the aryl substituent. Herein, we report the synthesis of the new primary phosphines 2-*i*-$PrC_6H_4PH_2$ and 2-*t*-$BuC_6H_4PH_2$ as well as the bis(trimethylsilyl)phosphines 2-*i*-$PrC_6H_4P(SiMe_3)_2$ and 2-*t*-$BuC_6H_4P(SiMe_3)_2$. This synthetic methodology is amenable to the isolation of multigram quantities of material from commercially available starting materials.

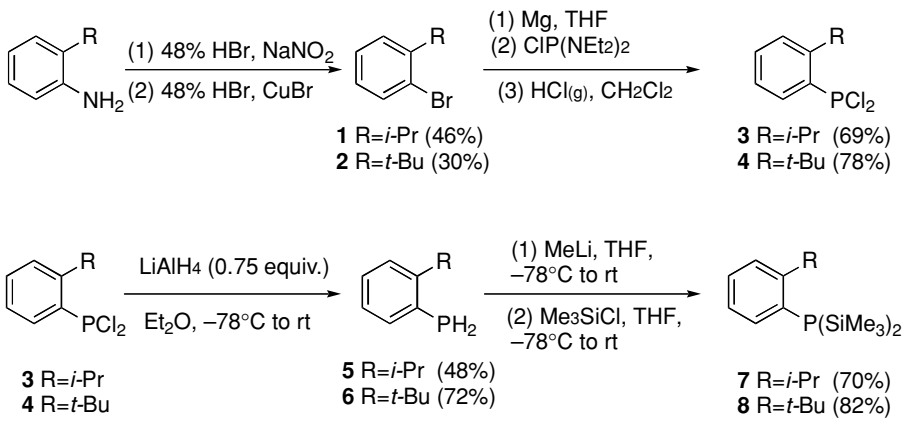


SCHEME 2

RESULT AND DISCUSSION

The synthesis starts with aryl bromides **1** and **2**, prepared from the corresponding commercially available aniline derivatives using a Sandmeyer reaction [30] (Scheme 3). The addition of magnesium metal to the aryl bromide (**1** or **2**) in tetrahydrofuran (THF) generates the respective Grignard reagents, which are then treated with $ClP(NEt_2)_2$ [31]. The use of diethylamino-protected chlorophosphine instead of PCl_3 ensures that only a single aryl-substitution occurs at phosphorus. Analysis of the product by ^{31}P NMR spectroscopy confirms that only a single product is formed, and the chemical shift is consistent with its formulation as 2-$RC_6H_4P(NEt_2)_2$ (R = *i*-Pr: $\delta = 94$; R = *t*-Bu: $\delta = 93$). Although it is possible to isolate the bis(aminophosphines), we found it more convenient to simply treat the crude product with anhydrous hydrogen chloride in CH_2Cl_2 to remove the diethylamino protecting groups. The dichlorides **3** and **4** are obtained in satisfactory overall yields after distillation (69% and 78%, respectively). The products were analyzed by ^{31}P NMR spectroscopy (**3**: $\delta =$ 164, **4**: $\delta = 166$). These chemical shifts are similar to related dichloroarylphosphines such as $MesPCl_2$ ($\delta = 167$) [32].

Reduction of the dichlorides **3** and **4** using $LiAlH_4$ affords primary phosphines **5** and **6** in good isolated yield (70% and 82%, respectively). Although phosphine **5** has previously been mentioned, its synthesis and characterization were not reported [33].



SCHEME 3

Analysis of the products using ^{31}P NMR spectroscopy revealed triplet resonances that are characteristic of primary phosphines [**5**: $\delta = -127$ (t, $^1J_{PH} = 203$ Hz), **6**: $\delta = -107$ ppm (t, $^1J_{PH} = 202$ Hz)]. Interestingly, these signals are shifted downfield when compared to $MesPH_2$(−149 ppm, t, $^1J_{PH} = 203$ Hz) [32] and the chemical shift for **6** is closer to alkyl phosphines such as *t*-$BuPH_2$ (−80 ppm, t, $^1J_{PH} = 180$ Hz) and (*cyclo*-C_6H_{11})PH_2 (−111 ppm, t, $^1J_{PH} = 187$ Hz) [32]. Compounds **5** and **6** were further characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and mass spectrometry, each of which supported the assigned structures. Owing to the difficulty handling pyrophoric phosphines **5** and **6**, elemental microanalysis could not be accurately obtained.

The final step in the preparation of bis(trimethylsilyl)phosphines **7** and **8** involves treating **5** or **6** with MeLi (2 equiv) followed by silylation using Me_3SiCl. The desired bis(trimethysilyl)phosphines were isolated in reasonable yield after distillation (**7**: 48%, **8**: 72%). Compound **7** and **8** were characterized by ^{31}P, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy, low-resolution and high-resolution mass spectrometry, and elemental analysis. Interestingly, the ^{31}P chemical shift of **7** ($\delta = -153$) is similar to $MesP(SiMe_3)_2$ ($\delta = -164$), whereas that for **8** ($\delta = -135$) is similar to alkyl-substituted *cyclo*-$C_6H_{11}P(SiMe_3)_2$ ($\delta = -139$). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** and **8** are consistent with the proposed structures.

SUMMARY

A synthetic methodology has been developed to prepare new moderately bulky phosphines from commercially available 2-substituted anilines. The chlorides, hydrides, and silylides of 2-*i*-PrC_6H_4- and 2-*t*-BuC_6H_4-substituted phosphines have been prepared and fully characterized spectroscopically. This synthetic route is amenable to the preparation of multigram quantities of product in a linear fashion. The new bis(trimethylsilyl)arylphosphines (**7** and **8**) are of interest for the synthesis of new phosphaalkenes for applications as supporting ligands for metal-catalyzed organic transformations.

EXPERIMENTAL

General Procedures

All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Hexanes and CH_2Cl_2 were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was distilled from sodium/benzophenone ketyl. Reagents, 2-*i*-$PrC_6H_4NH_2$, 2-*t*-$BuC_6H_4NH_2$, Mg, Me_3SiCl, and $LiAlH_4$ were purchased from Aldrich and used as received. Anhydrous HCl was obtained from BOC Gases and used as received. MeLi in Et_2O was purchased from Aldrich and titrated with *N*-benzylbenzamide prior to use.

^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. 85% H_3PO_4 was used as an external standard ($\delta = 0.0$ for ^{31}P). ^1H NMR spectra were referenced to residual protonated solvent, and $^{13}C\{^1H\}$ NMR were referenced to the deuterated solvent. Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV).

*2-i-PrC$_6$H$_4$PCl$_2$ (**3**).* To a solution of Mg (2.97 g, 122 mmol) in THF (150 mL), 2-*i*-PrC$_6$H$_4$Br (20.3 g, 102 mmol) was added. After 30 min, the Grignard activated and the solution was refluxed for an additional 2 h. The mixture was cooled to r.t. and treated with ClP(NEt$_2$)$_2$ [31] (23.6 g, 112 mmol) and washed with THF (5 mL). The solvent was removed in vacuo, and the phosphine was extracted with hexanes (1 × 100 mL, 2 × 80 mL). The hexanes were removed in vacuo leaving crude 2-*i*-PrC$_6$H$_4$P(NEt$_2$)$_2$ as a colorless liquid with ^{31}P NMR singlet resonance of 94 ppm. The crude solution of 2-*i*-PrC$_6$H$_4$P(NEt$_2$)$_2$ in CH$_2$Cl$_2$ (150 mL) was treated with gaseous dry HCl, and the mixture became darker, cloudy, and then clear. ^{31}P NMR analysis of an aliquot removed from the reaction mixture indicated two signals at 221 ppm (PCl$_3$) and 167 ppm (2-*i*-PrC$_6$H$_4$PCl$_2$). CH$_2$Cl$_2$ was evaporated in vacuo. The yellow solid was extracted with toluene (3 × 60 mL), filtered, and the solvent was removed in vacuo. The crude product was purified by vacuum distillation 95°C (0.01 mmHg) to afford **3** (15.5 g, 69%) as a colorless liquid.

^{31}P NMR (162 MHz, CDCl$_3$): δ 164 (s); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15–8.11 (m, 1H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 2H), 3.76 (sept, $^3J_{HH}$ = 7 Hz, 1H), 1.36 (d, $^3J_{HH}$ = 7 Hz, 6 H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 151.8 (d, J_{PC} = 31 Hz), 137.2 (d, J_{PC} = 56 Hz), 133.1, 130.6 (d, J_{PC} = 7 Hz), 127.2 (d, J_{PC} = 1 Hz), 125.7 (d, J_{PC} = 34 Hz), 31.1 (d, J_{PC} = 33 Hz), 24.4; MS (EI): *m/z* (%) 224, 222, 220 [7, 42, 66, M$^+$], 209, 207, 202 [3, 15, 23, M-CH$_3$], 187, 186, 185 [10, 9, 32, M-Cl]; Anal Calcd for C$_9$H$_{11}$Cl$_2$P: C, 48.90; H, 5.02; found: C, 48.84; H, 5.02.

*2-t-BuC$_6$H$_4$PCl$_2$ (**4**).* Same procedure as described above for **3**. Used 2-*t*-BuC$_6$H$_4$Br (8.47 g, 40 mmol), Mg (1.16 g, 48 mmol), and PCl(NEt$_3$)$_2$ (9.27 g, 44 mmol). The crude product was purified by vacuum distillation 110°C (0.01 mmHg) to afford **4** (7.4 g, 78%) as a colorless liquid.

^{31}P NMR (121 MHz, CDCl$_3$): δ 166 (s); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.36–8.31 (m, 1H), 7.46–7.36 (m, 3H), 1.57 (s, 9H); ^{13}C{^{1}H} NMR (121 MHz, CDCl$_3$): δ 153.5 (d, J_{PC} = 28 Hz), 140.4 (d, J_{PC} = 68 Hz), 134.9, 132,4, 127.5, 125.2, 37.0, 33.7; HRMS (EI): Cacld for C$_{10}$H$_{13}$Cl$_2$P 234.0132; found: 234.0131; MS (EI): *m/z* (%) 236, 235, 234 [43, 24, 68, M$^+$], 221, 220, 219 [18, 4, 27, M-Me], 201, 200, 199 [14, 10, 45, M-Cl], 147 [100, M-CH$_5$Cl$_2$], 133 [22, M-PCl$_2$]; Anal Calcd for C$_{10}$H$_{13}$Cl$_2$P: C, 51.09; H, 5.57; found: C, 50.97; H, 5.60.

*2-i-PrC$_6$H$_4$PH$_2$ (**5**).* To a cooled (−78°C) solution of LiAlH$_4$ (2.1 g, 56 mmol) in Et$_2$O (300 mL), a solution of **3** (15.5 g, 70 mmol) in Et$_2$O (15 mL) was added. The cooling bath was removed, and the solution was warmed to room temperature. ^{31}P NMR analysis of an aliquot removed from the reaction mixture showed triplet resonance at −129 ppm. Degassed water (100 mL) was added to quench residual aluminum hydride. (*Caution:* Extreme care should be taken when adding the first few milliliters of water since quenching is highly exothermic and H$_2$ is evolved.) The ether layer was removed, and the aqueous layer extracted with Et$_2$O (150 mL, 100 mL). The organic layers were combined, and the solvent removed in vacuo. The crude product was purified by vacuum distillation 60°C (0.01 mmHg) to afford **5** (7.5 g, 70%) as colorless liquid. (*Caution:* The product is pyrophoric and very malodorous.)

^{31}P NMR (162 MHz, CDCl$_3$): δ −127 (t, J_{PH} = 203 Hz); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53–7.48 (m, 1H), 7.34–7.26 (m, 2H), 7.13–7.06 (m, 1H), 3.96 (d, J_{PH} = 203 Hz, 2H), 3.28 (sept, $^3J_{HH}$ = 7 Hz, 1H), 1.29 (d, $^3J_{HH}$ = 7 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 152 (d, J_{PC} = 13 Hz), 136 (d, J_{PC} = 7 Hz), 129, 128 (d, J_{PC} = 8 Hz), 126 (d, J_{PC} = 3 Hz), 125 (d, J_{PC} = 3Hz) 33 (d, J_{PC} = 15 Hz), 24; MS (EI): *m/z* (%) 153, 152 [100, 11, M$^+$], 138, 137 [33, 4, M-Me] 120, 119 [13, 4, M-PH$_2$], 111, 110 [82, 9, M-C$_3$H$_6$], 91 [40, C$_7$H$_7$].

*2-t-BuC$_6$H$_4$PH$_2$ (**6**).* Same procedure as described above for **5**. Used **4** (7.2 g, 31 mmol) and LiAlH$_4$ (0.873 g, 23 mmol). The crude product was purified by vacuum distillation 60°C (0.01 mmHg) to afford title compound (4.17 g, 82%) as a colorless liquid.

^{31}P NMR (162 MHz, CDCl$_3$): δ −107 (t, $^1J_{PH}$ = 202 Hz); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58–7.53 (m, 1H), 7.47–7.42 (m, 1H), 7.29–7.23 (m, 1H), 7.11–7.05 (m, 1H), 4.21 (d, $^1J_{PH}$ = 203 Hz, 2H), 1.52 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 154.3 (d, J_{PC} = 15 Hz), 140.0, 128.7, 127.8 (d, J_{PC} = 17 Hz), 126.6 (d, J_{PC} = 5 Hz), 125.8, 36.9, 31.3 (d, J_{PC} = 11 Hz); HRMS calcd for C$_{10}$H$_{15}$P: 166.0911; found: 166.0908; MS (EI): *m/z* (%) 167, 166 [7, 62, M$^+$], 166 [100, M-H], 152, 151 [5, 56, M-Me], 134, 133 [3, 16, M-PH$_2$], 110, 109 [13, 44, M-*t*-Bu], 57 [28, *t*-Bu].

*2-i-PrC$_6$H$_4$P(SiMe$_3$)$_2$ (**7**).* To a cooled solution (−78°C) of **5** (7.0 g, 46 mmol) in THF (100 mL), MeLi in Et$_2$O (1.45 M, 70 mL, 101 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h whereafter the solution was cooled (−78°C) and treated with Me$_3$SiCl (13.5 mL, 106 mmol). ^{31}P NMR analysis of an aliquot removed from the reaction mixture revealed

the presence of 2-*i*-$PrC_6H_4P(SiMe_3)_2$ at −153 ppm. Often, after the first lithiation a mixture of 2-*i*-$PrC_6H_4P(SiMe_3)_2$ and 2-*i*-$PrC_6H_4PH(SiMe_3)$ was observed. In this instance, the reaction mixture was relithiated (20 mL) and silylated (3.6 mL) following the above-mentioned procedure. Typically, after one relithiation **7** was formed quantitatively (^{31}P NMR spectroscopy). The solvent was removed in vacuo. The yellow solid was extracted with hexanes (2 × 100 mL, 50 mL), filtered, and the solvent was removed. The crude product was purified by vacuum distillation (113°C, 0.01 mmHg), affording title compound (6.6 g, 48%) as a colorless liquid.

^{31}P NMR (162 MHz, $CDCl_3$): δ −153 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.46 (m, 1H), 7.34–7.25 (m, 2H), 7.10–7.04 (m, 1H), 3.98 (sept, $^3J_{HH} = 7$ Hz, 1H), 1.25 (d, $^3J_{HH} = 7$ Hz, 6H), 0.30 (s, 9H), 0.28 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.6 (d, $J_{PC} = 21.5$ Hz), 138.5 (d, $J_{PC} = 6$ Hz), 130.3 (d, $J_{PC} = 11.5$ Hz), 128.1, 125.6 (d, $J_{PC} = 6$ Hz), 124.9, 32.2 (d, $J_{PC} = 24$ Hz), 23.9, 1.6, 1.4; HRMS calcd for $C_{13}H_{29}PSi_2$: 296.1546; found: 296.1547; MS (EI): *m/z* (%) 297, 296 [6, 21, M^+], 282, 281 [2, 6, M-Me], 224, 223 [4, 10, M-$SiMe_3$], 75, 74, 73 [4, 8, 100, $SiMe_3$]; Anal Calcd for $C_{15}H_{29}PSi_2$: C, 60.76; H, 9.86; found: C, 60.42; H, 9.84.

2-*t*-*BuC*$_6$*H*$_4$*P*(*SiMe*$_3$)$_2$ (**8**). Same procedure as described above for **7**. Used **6** (4.1 g, 25 mmol), MeLi in Et_2O (1.5 M, 33 mL, 50 mmol) and TMSCl (6.3 mL, 50 mmol). The crude product was purified by vacuum distillation (130°C, 0.01 mmHg) to afford title compound (5.65 g, 72%) as a colorless liquid.

^{31}P NMR (162 MHz, $CDCl_3$): δ −134 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.53 (m, 1H), 7.48–7.43 (m, 1H), 7.25–7.19 (m, 1H), 7.09–7.03 (m, 1H), 1.62 (d, $J_{PH} = 1$ Hz 9H), 0.29 (s, 9H), 0.28 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.7 (d, $J_{PC} = 18$ Hz), 142.6 (d, $J_{PC} = 6$ Hz), 130.8 (d, $J_{PC} = 22$ Hz), 127.7, 126.6 (d, $J_{PC} = 8$ Hz), 124.6, 37.4, 32.0 (d, $J_{PC} = 11$ Hz), 1.9, 1.8; HRMS calcd for $C_{16}H_{31}PSi_2$: 310.1702; Found: 310.1701; MS (EI): *m*/z (EI) 312, 311, 310 [2, 9, 32, M^+], 296, 295 [3, 9, M-Me], 239, 238, 237 [4, 10, 49, M-$SiMe_3$], 74, 73 [7, 100, $SiMe_3$]; Anal Calcd for $C_{16}H_{31}PSi_2$: C, 61.88; H, 10.06; found: C, 61.90; H, 10.09.

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